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THE CORRELATED HARTREE-FOCK EQUATIONS AND THE GENERALISED DENSITY MATRICES

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1. Introduction

One of the important problems of molecular chemistry concerns the evaluation of the correlation energy of molecules and the study, in general, of correlation effects in many-electron systems. The motions of the electrons in atomic or molecular systems are not independent of each other but are dependent on (or correlated with) the positions and spins of the other electrons. This correlation now is of two kinds—the first one arising from the limitations imposed by the Pauli Exclusion Principle which forbids two electrons of the same spin to stay in the same state, and the second kind arising from the strong Coulomb repulsion experienced by any two electrons when they try to approach each other closely.

The standard method of solving many-electron problems in quantum mechanics is by means of the Hartree-Fock equations, which are the variational equations of the Hamiltonian operator for a wave function that is a determinantal expression in the one-electron orbitals. Since the wave function is a determinant in the one-electron orbitals of the different electrons of the system, it will vanish when the co-ordinates of any two electrons having the same spin become identical and thus the Pauli Principle is implicit in this scheme. Or in other words, the Hartree-Fock equations suggest and bring within their scheme the correlation between electrons of the same spin, but because of the one-electron approximation they fail adequately to take into account of the Coulomb repulsion effects between the electrons. Experience has in fact shown that the H. F. equations give a much higher value for the energy of a molecular system than the experimentally observed one; this is to be expected because the H.F. equations neglect the Coulomb correlation between the electrons and would consequently contribute a much higher value for the repulsion energy of the system than is actually possible.

Coulomb correlation between the electrons can be brought into the theoretical formalism in several ways, but the simplest and most direct method

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of them all is to multiply the wave function by a correlation factor $g(r_{12}, r_{13} \ldots)$ which is symmetric in the inter-electronic distances $r_{12}, r_{13} \ldots\ldots$, etc. Such a method has been found to be very effective for two electron systems like He^+ ions and the hydrogen molecule, and it has been shown by Hylleraas, Löwdin and Redei that by using simple correlation factors of the type $e^{ar_{12}}$ or $(1 + ar_{12})$, the energy for the Helium atom could be improved much beyond the value yielded by the H.F. equations. The introduction of the correlation factor modifies the field in which an electron is moving, and each electron moves in the average potential field of the remaining electrons subject to the condition that no two electrons can approach each other closely. The wave functions of the different electrons moving in such a correlated field will be different from the one electron orbitals obtained by solving the H.F. equations, and an important problem in the study of correlation effects is to determine the one-electron orbitals in this case. The equations determining these orbitals are given in Section 4 by making use of a formula given by Löwdin; in Section 8 we give the correlated Hartree-Fock equations for non-stationary systems. In Section 4, we have given the integro-differential equations satisfied by the generalised density matrices, and from these it is shown that one can obtain an expression for the energy matrix of the system which will be useful in determining a correlated Thomas-Fermi destribution. In Section 7, some remarks are made on the effects of correlation by a study of the general equations for the simple case of two electron systems.

2. Density Matrices

Let $\Psi(x_1, x_2, \ldots, x_N)$ be the normalised eigenfunction of the system so that we have

$$\int \Psi^* \Psi d\tau = 1 \tag{1}$$

where

$$\int d\tau = \int dx_1 dx_2 \ldots dx_N$$

denotes integration over all space co-ordinates and summation over spin co-ordinates. The generalised density matrices have been defined by Löwdin as follows:

$$\Gamma(x_1' \mid x_1) = N \int \Psi^* (x_1' x_2 \ldots x_N) \Psi (x_1 x_2 \ldots x_N) dx_2 \ldots dx_N$$

$$\Gamma(x_1' x_2' \mid x_1 x_2)$$

$$= \binom{N}{2} \int \Psi^*(x_1' x_2' x_3 \ldots x_N)\, \Psi(x_1 x_2 \ldots x_N)\, dx_3 \ldots dx_N$$

$$\Gamma(x_1' x_2' \ldots x_p' \mid x_1 x_2 \ldots x_p)$$

$$= \binom{N}{p} \int \Psi^*(x_1' x_2' \ldots x_p' x_{p+1} \ldots x_N)\ \ \Psi(x_1 \ldots x_N)$$

$$\times\, dx_{p+1} \ldots dx_N. \tag{2}$$

For a system of N electrons, Ψ is an anti-symmetric function of the co-ordinates (space as well as spin) of the electrons and we choose for Ψ the following determinant:

$$\Psi = (N!)^{-\frac{1}{2}} \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) & \ldots & \psi_N(x_1) \\ \psi_1(x_2) & \psi_2(x_2) & \ldots & \psi_N(x_2) \\ \ldots\ldots\ldots & \ldots\ldots\ldots & \ldots & \ldots\ldots\ldots \\ \psi_1(x_N) & \psi_2(x_N) & \ldots & \psi_N(x_N) \end{vmatrix}. \tag{3}$$

We assume for the sake of simplicity that the ψ's form an ortho-normal system so that we have

$$\int \psi_i^*(x)\, \psi_k(x)\, dx = \delta_{ik}. \tag{4}$$

Now

$$\Psi^* \Psi = \frac{1}{N!}\, \rho = \frac{1}{N!} \det \| \rho_{ij} \tag{5}$$

where

$$\rho_{ij} = \sum_{k=1}^{N} \psi_k^*(x_i)\, \psi_k(x_j).$$

For future applications, we need also the quantity ρ'_{ij} defined by

$$\rho'_{ij} = \sum_{k=1}^{N} \psi_k^*(x_i')\, \psi_k(x_j). \tag{6}$$

Since the ψ's form an ortho-normal set, we have

$$\int \rho'_{iN} \rho_{Nj}\, dx_N = \rho'_{ij}. \tag{7}$$

The integral of ρ over the co-ordinates of the various electrons has been given in Mott and Sneddon.[5] By adopting a similar procedure for the evaluation of the integrals and making use of (7), we can show that

$$\Gamma(x_1' \mid x_1) = \rho'_{11} = \rho_1'$$

$$\Gamma(x_1'x_2' \mid x_1x_2) = \frac{1}{2!}\begin{vmatrix} \rho'_{11} & \rho'_{12} \\ \rho'_{21} & \rho'_{22} \end{vmatrix} = \frac{1}{2!}\rho_2'$$

$$\Gamma(x_1'x_2' \ldots x_p' \mid x_1 \ldots x_p) = \frac{1}{p!}\begin{vmatrix} \rho'_{11} & \cdots & \rho'_{1p} \\ \cdots & \cdots & \cdots \\ \rho'_{p1} & \cdots & \rho'_{pp} \end{vmatrix} = \frac{1}{p!}\rho'_p \qquad (8)$$

where we have written ρ'_p for the determinant in the above line containing p rows and p columns.

There are several problems that deal with time-dependent processes, and the density matrices in such cases can be defined analogous to (2). Thus if $\Psi(x_1x_2 \ldots x_Nt)$ is the normalised time-dependent wave function for the system, we define the density matrix of order p as follows:—

$$\Gamma(x_1'x_2' \ldots x_p't' \mid x_1x_2 \ldots x_pt)$$

$$= \binom{N}{p} \int \Psi^*(x_1'x_2' \ldots x_p'x_{p+1} \ldots x_Nt')\ \Psi(x_1 \ldots x_Nt)\ dx_{p+1} \ldots dx_N. \qquad (2\,a)$$

If as before we choose for Ψ a determinant built from one-electron orbitals so that

$$\Psi(x_1 \ldots x_Nt) = (N!)^{-\frac{1}{2}} \det\{\psi_1(x_1t) \ldots \psi_N(x_Nt)\} \qquad (3\,a)$$

where the orbitals $\psi_1, \psi_2, \ldots, \psi_N$ satisfy the orthonormality conditions

$$\int \psi_i^*(xt)\,\psi_k^*(xt)\,dx = \delta_{ik} \qquad (4\,a)$$

then it follows that

$$\Gamma(x_1'x_2' \ldots x_p't' \mid x_1 \ldots x_pt) = \frac{\rho_p'}{p!}. \qquad (8\,a)$$

In the above

$$\rho_p' = \begin{vmatrix} \rho'_{11} & \rho'_{12} \cdots \rho'_{1p} \\ \rho'_{21} & \rho'_{22} \cdots \rho'_{2p} \\ \cdots & \cdots \\ \rho'_{p1} & \rho'_{p2} \cdots \rho'_{pp} \end{vmatrix};$$

and

$$\rho'_{ij} = \rho'(x_i't'; x_jt) = \sum_k \psi_k^*(x_i't')\,\psi_k(x_jt) \qquad (6\,a)$$

Further if $G(x_1x_2 \ldots x_l)$ is a symmetric function of the co-ordinates o l electrons, it can be shown (see Appendix I for proof) that

$$\frac{\binom{N}{l}}{N!}\int G(x_1x_2 \ldots x_l)\frac{\partial\rho'_N}{\partial t}\,dx_1 \ldots dx_N$$

$$= \frac{1}{l!}\int G(x_1 \ldots x_l)\frac{\partial\rho'_{l+1}}{\partial t}\,dx_1 \ldots dx_{l+1} + \frac{(N-l-1)}{l!}$$

$$\times \int \frac{G(x_1 \ldots x_l)}{dx_1 \ldots dx_{l+1}} \begin{vmatrix} \rho'_{11} \ldots\ldots\ldots \rho_{1l}' & \rho'_{1l+1} \\ \ldots\ldots\ldots\ldots\ldots\ldots \\ \rho'_{l1} \ldots\ldots\ldots \rho'_{ll} & \rho'_{ll+1} \\ \frac{\partial\rho'_{l+1,1}}{\partial t} \quad \ldots \quad \frac{\partial\rho'_{l+1,l}}{\partial t} & 0 \end{vmatrix}. \qquad (9)$$

3. The Energy of the System

The Hartree-Fock equations are the Euler differential equations of the variational principle

$$\delta \int \Psi^* H \Psi d\tau = 0. \qquad (10)$$

In view of the one-electron approximation, the Hartree-Fock equations do not adequately take into account of the Coulomb correlation, and we shall, following Löwdin, take the correlated wave function of the system as the product of a correlation factor which is a symmetric function of the inter-electronic distances and the Slater determinant. The wave function Φ for the system then becomes

$$\Phi = g(r_{12}, {}_1r_3 \ldots)\,\Psi. \qquad (11)$$

For g, we shall choose the form

$$g(r_{12}, r_{13} \ldots) = \alpha + \beta \sum_{\substack{ij \\ i<j}} f(r_{ij}) \qquad (11\,a)$$

where the functions $f(r_{ij})$ are supposed to be known. The simple functions r_{12} or $(e^{ar_{12}} - 1)$ may be regarded as good choices for the correlation function $f(r_{12})$. One of the constants, say α, can be determined from the condition

$$\int \Phi^* \Phi d\tau = 1 \qquad (11\,b)$$

and β can then be chosen as the best parameter minimising the energy. Now the best one-electron wave functions $\psi_i(x)$ $(i = 1, 2, \ldots, N)$ can be determined from the variational principle

$$\delta W = \delta \int \Phi^* H \Phi d\tau = \delta \int \Psi^* H_c \Psi d\tau = 0 \tag{12}$$

where

$$H_c = gHg. \tag{13}$$

Before writing down the variational equations we shall first fix the form of H_c.

Now

$$\begin{aligned} H_c &= \left\{ \alpha + \beta \sum_{\substack{ij \\ i<j}} f(r_{ij}) \right\} \left\{ \sum_{i=1}^{N} E_i + \tfrac{1}{2} \sum_{i,k}' F(x_i, x_k) \right\} \\ &\quad \times \left\{ \alpha + \beta \sum_{\substack{ij \\ i<j}} f(r_{ij}) \right\} \\ &= \alpha^2 \left\{ \sum_{i=1}^{N} E_i + \tfrac{1}{2} \sum_{ik}' F(x_i, x_k) \right\} \\ &\quad + \alpha\beta \sum_{i=1}^{N} \sum_{\substack{s,t \\ s<t}} [f(r_{st}), E(i)] \\ &\quad + 2\alpha\beta \sum_{\substack{st \\ s<t}} \sum_{\substack{ik \\ i<k}} f(r_{st}) F(x_i, x_k) \\ &\quad + \beta^2 \left\{ \sum_{\substack{st \\ s<t}} \sum_{i=1}^{N} \sum_{\substack{s't' \\ s'<t'}} f(r_{st}) E(i) f(r_{s't'}) \right. \\ &\quad \left. + \sum_{\substack{st \\ s<t}} \sum_{\substack{ik \\ i<k}} \sum_{\substack{s't' \\ s'<t'}} f(r_{st}) F(x_i, x_k) f(r_{s't'}) \right\} \\ &= T_1 + T_2 + T_3 + T_4. \end{aligned} \tag{14}$$

In the above $[u, v]$ denotes the operator $(uv + vu)$. Consider now the term T_3. The summation here contains $N^2(N-1)/2$ terms. Of these, the number of terms for which i, s and t are different is $3\binom{N}{3}$ while the number of terms involving two indices only is $N(N-1)$.

Let us write

$$T_2(i,s) = \alpha\beta\,[f(r_{is}), E(i) + E(s)]$$

$$T_2(i,s,t) = \alpha\beta\,\{[f(r_{st}), E(i)] + [f(r_{it}), E(s)] + [f(r_{is}), E(t)]\}. \quad (15\,a)$$

Then

$$T_2 = \sum_{\substack{ij \\ i<s}} T_2(i,s) + \sum_{\substack{i,st \\ i<s<t}} T_2(i,s,t). \quad (15\,b)$$

Consider next T_3. The summation over i, k, $(i<k)$ and s, t $(s<t)$ contains $N^2(N-1)^2/4$ terms. Of these, there are $\binom{4}{2}$ $\binom{N}{4}$ terms of the type $r_{st}\,F(x_i, x_k)$ involving four different indices, $6\binom{N}{3}$ terms of the type $F(x_i, x_t)\,r_{is}$ involving three different indices and $\binom{N}{2}$ terms of the type $r_{ik}\,F(x_i, x_k)$ involving two indices only. If we write

$$T_3(i,s) = 2\alpha\beta f(r_{is})\,F(x_i, x_s)$$

$$T_3(i,s,t) = 2\alpha\beta\,[F(x_i, x_t)\big(f(r_{is}) + f(r_{st})\big) + F(x_i, x_s) \times \big(f(r_{it}) + f(r_{st})\big) + F(x_s, x_t)\big(f(r_{si}) + f(r_{ti})\big)]$$

$$T_3(i,k,s,t) = 2\alpha\beta\,[f(r_{ik})\,F(x_s, x_t) + \text{five similar terms arising from the permutation of } i, k, s \text{ and } t],$$

then

$$T_3 = \sum_{\substack{ik \\ i<k}} T_3(i,s) + \sum_{\substack{ik,s \\ i<k<s}} T_3(i,s,t) + \sum_{\substack{i,k,s,t \\ i<k<s<t}} T_3(i,k,s,t). \quad (16)$$

We shall finally consider T_4. The first term of T_4, involving the operators E_i, consists of $N^3(N-1)^2/4$ terms and these can be split up into $30\binom{N}{5}$ terms containing five different indices, $48\binom{N}{4}$ terms containing four different indices, $21\binom{N}{3}$ terms containing three different indices and $2\binom{N}{2}$ terms containing two different indices. Similarly the second term of T_4 involving the operators $F(x_i, x_k)$ consists of $N^3(N-1)^3/8$ terms and the terms involving 2, 3, ..., 6 different indices in this are given by the relation

$$\frac{N^3(N-1)^3}{8} = 90\binom{N}{6} + 180\binom{N}{5} + 114\binom{N}{4} + 24\binom{N}{3} + \binom{N}{2}. \quad (17)$$

Let us denote by $T_4(i, s)$, $T_4(i, s, t)$, $T_4(i, k, s, t)$ ... $T_4(i, k, s, t, s', t')$ the terms in T_4 involving 2, 3, ..., 6 different indices. Then

$$T_4 = \sum_{\substack{i,s \\ i<s}} T_4(i, s) + \ldots + \sum_{\substack{ik \\ i<k<s<t}} \sum_{\substack{st \\ i<s<t<s'<t'}} \sum_{\substack{s't' \\ s'<t'}} T_4(i, k, s, t, s', t'). \quad (18)$$

We shall now write

$$H_c^1 = \alpha^3 E(i)$$

$$H_c^2(i, s) = \alpha^2 F(x_i, x_s) + T_2(i, s) + T_3(i, s) + T_4(i, s)$$

$$H_c^3(i, s, t) = T_2(i, s, t) + T_3(i, s, t) + T_4(i, s, t)$$

.....

$$H_c^6(i, k, s, t, s, t') = T_4(i, k, s, t, s', t'). \quad (19)$$

Then obviously

$$H_c = \sum_{i=1}^{N} H_c^1(i) + \frac{1}{2!} \sum_{i,s}' H_c^2(i, s) + \ldots + \frac{1}{6!} \times \sum_{ik,} \sum_{st,} \sum_{s't'} H_c^6(i, \ldots, t'). \quad (20)$$

We may note that the functions $H_c^1(x_1, x_2, \ldots, x_l)$ are symmetric in their arguments.

Now

$$W = \int \Phi^* H \Phi d\tau = \int \Psi^* H_c \Psi d\tau. \quad (21)$$

From (20) and (8) we have

$$W = \int H_c^1(x_1) \Gamma(x_1' \mid x_1)\, dx_1 + \int H_c^2(x_1 x_2) \Gamma(x_1' x_2' \mid x_1 x_2)\, dx_1 dx_2 + \ldots \int H_c^6(x_1 x_2 \ldots, x_6) \Gamma(x_1' \ldots x_6' \mid x_1 \ldots x_6)\, dx_1 \ldots dx_6. \quad (22)$$

where we are following the convention that, in the integrands, the operators $H_c^1(x_1)$, $H_c^2(x_1, x_2)$ ... operate only on the unprimed co-ordinates $x_1, \ldots, x_6$ and that, after these operations have been carried out, we have to put $x_1' = x_1$; $x_2' = x_2$; ...; $x_6' = x_6$ before the integrations.

We see from (22) that the energy of the system is a functional of the density matrices alone.

4. The Correlated Hartree-Fock Equations

Löwdin has determined the one-electron functions $\psi_1, \psi_2, \ldots, \psi_N$ that make the determinant Ψ the 'best' approximation for the eigenvalue problem

$$\Omega_{op.}\,\Psi = W\Psi \tag{23}$$

where $\Omega_{op.}$ is a many-particle operator expressible as

$$\Omega_{op.} = \Omega_0 + \sum_i \Omega_i + \frac{1}{2!}\sum_{ij}{}' \Omega_{ij} + \frac{1}{3!}\sum_{ijk}{}' \Omega_{ijk} + \ldots . \tag{24}$$

The prime in the above indicates that the summation excludes terms having two or more indices equal.

The equations determining the functions $\psi_1, \psi_2, \ldots, \psi_N$ are given by

$$\Omega_1\psi_k(x_1) + \int \Omega_{12} \begin{vmatrix} \psi_k(x_1) & \psi_k(x_2) \\ \rho(x_2', x_1) & \rho(x_2'x_2) \end{vmatrix} dx_2$$

$$+ \frac{1}{2!}\int \Omega_{123} \begin{vmatrix} \psi_k(x_1) & \psi_k(x_2) & \psi_k(x_3) \\ \rho(x_2'x_1) & \rho(x_2'x_2) & \rho(x_2'x_3) \\ \rho(x_3'x_1) & \rho(x_3'x_2) & \rho(x_3'x_2) \end{vmatrix} dx_2 dx_3$$

$$= \sum_{i=1}^{N} \lambda_{ki}\psi_i(x_1). \tag{25}$$

Now H_c is a many-particle operator similar to (24) and thus the best one-electron orbitals that minimise the energy of the system can be obtained from (25) by replacing $\Omega_{op.}$ by H_c. By expanding the determinants in (25) along the first row and denoting by $\rho'_{1;1j}$ the co-factor of ρ'_{1j} in ρ'_1, we can write the integro-differential equations determining the correlated orbitals as

$$H_c^1(x_1)\,\psi_k(x_1) + \sum_{l=2}^{6} \frac{1}{(l-1)!}\int H_c^l(x_1 x_2 \ldots x_l)$$

$$\times \sum_{j=1}^{l} \rho'_{1;1j}\psi_k(x_j)\, dx_2 \ldots dx_l$$

$$- \sum_{i=1}^{N} \lambda_{ki}\psi_i(x_1) = 0 \qquad (k = 1, 2, \ldots, N). \tag{26}$$

The conjugate complex of the above equation is given by

$$\mathrm{H_c}^1(x_1)\,\psi_k^*(x_1) + \sum_{l=2}^{6} \frac{1}{(l-1)!} \int \mathrm{H_c}^l(x_1 \ldots x_l) \times \sum_{j=1}^{l} \rho'^*{}_{l;\,1j}\psi^*{}_k(x_j)\,dx_2 \ldots dx_l - \sum_{i=1}^{N} \lambda_{ik}\psi_i^*(x_1) = 0 \tag{27}$$

Equations (26) determine the correlated orbitals $\psi_i(x_i)$. They are a generalisation of the Hartree-Fock equations and since they explicitly take into account of correlation effects, they can be expected to give better theoretical values for physical parameters like energy, than the simple Hartree-Fock system of equations.

From (26) we have

$$\lambda_{ki} = \sum_{l=1}^{6} \frac{1}{(l-1)!} \int \psi_i^*(x_1)\,\mathrm{H_c}^l(x_1 \ldots x_l) \times \sum_{j=1}^{l} \rho'_{l;\,1j}\psi_k(x_j)\,dx_1 \ldots dx_l \tag{28}$$

and from (27) we see that

$$\lambda_{ki} = \lambda^*{}_{ik}. \tag{29}$$

As in the H.F. scheme we see that the λ_{ki} are a set of arbitrary constants forming a Hermitean matrix. Again as in the H.F. scheme, the set of orbitals $\psi_1, \psi_2, \ldots, \psi_N$ are not uniquely determined as the equations (26) are invariant under an orthogonal transformation of these functions. The elements ρ'_{ij} of the density matrices (and consequently the density matrices themselves) are, however, uniquely determined.

Multiplying (26) by $\psi_k^*(x_1')$, summing over k and remembering that

$$\frac{1}{l!} \sum_{j=1}^{l} \rho'_{l;\,1j}\rho'_{1j} = \Gamma(x_1' \ldots x_l' \mid x_1 \ldots x_l) \tag{30}$$

we get from (26), (28) and (30) that

$$\sum_{l=1}^{6} l \int \mathrm{H_c}^l (x_1 \ldots x_l)\, \Gamma(x_1', x_2', \ldots, x_l' \mid x_1 \ldots x_l)\, dx_2 \ldots dx_l$$

$$= \sum_{l=1}^{6} \frac{1}{(l-1)!} \int \rho_{\mu 1} \mathrm{H_c}^l (x_\mu x_2 \ldots x_l)$$

$$\times \begin{vmatrix} \rho'_{1\mu} & \rho'_{12} \cdots \rho'_{1l} \\ \rho'_{2\mu} & \rho'_{22} \cdots \rho'_{2l} \\ \cdots\cdots\cdots\cdots \\ \rho'_{l\mu} & \rho'_{l2} \cdots \rho'_{ll} \end{vmatrix} dx_\mu dx_2 \ldots dx_l. \tag{31}$$

Multiplying (26) by $\psi_k^*(x_a)$ and subtracting from it the corresponding equation for the conjugate of $\psi_k(x_a)$ multiplied by $\psi_k(x_1)$ and summing over k, one gets

$$\sum_{l=1}^{6} \frac{1}{(l-1)!} \int \mathrm{H_c}^l (x_1 \ldots x_l)$$

$$\times \begin{vmatrix} \rho'_{a1} & \rho'_{a2} \cdots \rho'_{al} \\ \rho'_{21} & \rho'_{22} \cdots \rho'_{2l} \\ \cdots\cdots\cdots\cdots \\ \rho'_{l1} & \rho'_{l2} \cdots \rho'_{ll} \end{vmatrix} dx_2 \ldots dx_l$$

$$= \sum_{l=1}^{6} \frac{1}{(l-1)!} \int \mathrm{H_c}^l (x_a \ldots x_l)$$

$$\times \begin{vmatrix} \rho'_{1a} & \rho'_{12} \cdots \rho'_{1l} \\ \rho'_{2a} & \rho'_{22} \cdots \rho'_{2l} \\ \cdots\cdots\cdots\cdots \\ \rho'_{la} & \rho'_{l2} \cdots \rho'_{ll} \end{vmatrix}^* dx_2 \ldots dx_l. \tag{32}$$

Equations (31) and (32) are integro-differential equations governing the density matrices. When correlation effects are neglected, we have $g = 1$ and therefore $\alpha = 1$ and $\beta = 0$. It can easily be verified that in this case equations (26) reduce to the ordinary Hartree-Fock equations. Further, if we write

$F(x_1, x_2) = e^2 / r_{12}$ and $B(x_1) = \int F(x_1, x_2)\, \rho(x_2, x_2)\, dx_2$, then equation (32) reduces to the well-known equation.[6]

$$\{E(x) + B(x) - E(x') - B(x')\}\, \rho(x, x') - \int [F(x, x'') - F(x', x'')]\, \rho(x, x'')\, \rho(x'', x')\, dx'' = 0. \tag{33}$$

If we write

$$E(x) = \frac{p^2}{2m} + V(x) = -\frac{h^2}{8\pi^2 m} \nabla_x^2 + V(x),$$

equation (31) becomes

$$\begin{aligned} &-\frac{h^2}{8\pi^2 m} \int \delta(x - x')\, \nabla_x^2 \rho(x', x)\, dx' + (V + B)\, \rho(x, x) \\ &= \int F(x, x')\, |\, \rho(x, x')\, |^2\, dx' + \int \rho(x', x)\, E(x')\, \rho(x, x')\, dx' \\ &\quad + \int F(x', x'')\, |\, \rho(x, x')\, |^2\, \rho(x'', x'')\, dx' dx'' \\ &\quad - \int F(x', x'')\, \rho(x', x)\, \rho(x, x'')\, \rho(x'', x')\, dx' dx''. \end{aligned} \tag{34}$$

The above equation can be used to determine the charge density $\rho(x, x)$ of the electron cloud of the atom.

5. The Energy Matrix

Let us now consider in greater detail the left-hand side of equation (32). We have

$$\begin{aligned} \text{L.H.S.} &= H_c^{1}(x_1)\, \rho'_{a1} + \sum_{l=2}^{6} \frac{1}{(l-1)!} \int \frac{H_c^{l}(x_1 \ldots x_l)}{dx_2 \ldots dx_l} \times \begin{vmatrix} \rho'_{a1} & \rho'_{a2} & \cdots & \rho'_{al} \\ \rho'_{21} & \rho'_{22} & \cdots & \rho'_{2l} \\ \cdots & \cdots & \cdots & \cdots \\ \rho'_{l1} & \rho'_{l2} & \cdots & \rho'_{ll} \end{vmatrix} \\ &= H_c^{1}(x_1)\, \rho'_{a1} + \sum_{l=2}^{6} \frac{1}{(l-1)!} \int H_c^{l}(x_1 \ldots x_l) \times \left\{ \rho'_{a1} \rho'_{l;\,11} + \sum_{k=2}^{l} \rho'_{ak} \rho'_{l;\,1k} \right\} dx_2 \ldots dx_l. \end{aligned} \tag{35}$$

Now since $H_c^l(x_1 \ldots x_l)$ is a symmetric function of $x_1, x_2, \ldots, x_l$, it can be seen by simple transpositions (x_2, x_k) $(k = 3, \ldots, l)$ of the integration variables $x_2, x_3, \ldots, x_k$ that the $(l-1)$ terms in the second summation of the above integral are all equal to $\int H_c^l(x_1 \ldots x_l)\, \rho'_{a2}\rho'_{l;12} dx_2 \ldots dx_l$.

Thus,

$$\text{L.H.S.} = H_c^1(x_1)\,\rho'_{a1} + \frac{1}{(l-1)!}\int H_c^l(x_1 \ldots x_l) \times \{\rho'_{a1}\rho'_{l;11} + (l-1)\,\rho'_{a2}\rho'_{l;12}\}\, dx_2 \ldots dx_l. \tag{36}$$

Now $\rho_{ij} = \rho(x_i, x_j) = \Sigma \psi_k^*(x_i)\,\psi_k(x_j)$ can be regarded as the (x_i, x_j)-th element of a continuous matrix ρ. We shall define a matrix $K(x_2, x_1)$ by means of the following relation:

$$K(x_2, x_1) = K^1(x_2, x_1) + \sum_{l=2}^{6} \frac{1}{(l-1)!} K^l(x_2, x_1) \tag{37}$$

where

$$K^1(x_2, x_1) = \int \delta(x_2 - \eta)\, H_c^1(\eta, p_\eta)\, \delta(\eta - x_1)\, d\eta$$

$$K^l(x_2, x_1) = \delta(x_2 - x_1)\, B^l(x_1) + (l-1)\int H_c^l(x_1 \ldots x_l) \times \rho'_{l;12} dx_3 \ldots dx_l; \tag{38}$$

and

$$B^l(x_1) = \int H_c^1(x_1 \ldots x_l)\, \rho'_{l;11}\, dx_2 \ldots dx_l. \tag{39}$$

We shall define the $(a1)$-th element of the product by ρK^l by

$$(\rho K^l)_{a1} = \int K^l(x_2, x_1)\, \rho(x_a, x_2)\, dx_2. \tag{40}$$

The definition is the same as the usual matrix multiplication law, but we take care to write $\rho(x_a, x_2)$ after the operator $K(x_2, x_1)$ so that the latter can operate on $\rho(x_a, x_2)$. We can then show the left-hand side of equation (32) to be the $(a1)$-th element of ρK. We have in fact

$$\begin{aligned}(\rho K^l)_{a1} &= \int \delta(x_1 - x_2)\, B^l(x_1)\, \rho(x_a, x_2)\, dx_2 \\ &\quad + (l-1)\int H_c^l(x_1 \ldots x_l)\, \rho'_{l;12}\rho'_{a2} \ldots dx_2 \ldots dx_l \\ &= B^l(x_1)\,\rho'_{a1} + \int H_c^l(x_1 \ldots x_l) \sum_{k=2}^{l} \rho'_{l;1k}\rho'_{ak} dx_2 \ldots dx_l \\ &= \int H_c^l(x_1 \ldots x_l) \begin{vmatrix} \rho'_{a1} & \rho'_{a2} & \cdots & \rho'_{al} \\ \rho'_{21} & \rho'_{22} & \cdots & \rho'_{2l} \\ \cdots & \cdots & \cdots & \cdots \\ \rho'_{l1} & & \cdots & \rho'_{ll} \end{vmatrix} dx_2 \ldots dx_l. \end{aligned} \tag{41}$$

Further $H_c^1(x_1)\rho'_{a1}$ is obviously the $(a!)$-th element of ρK^1. Thus the left-hand side of equation (32) is the (a')-th element of ρK. Similarly

$$\text{R.H.S.} = H_c^1(x_a)\rho'^*_{1a} + \sum_{l=2}^{6} \frac{1}{(l-1)!} \int H_c^l(x_a \ldots x_l) dx_2 \ldots dx_l \times \begin{vmatrix} \rho'_{1a} & \rho'_{12} & \cdots & \rho'_{1l} \\ \rho'_{2a} & \rho'_{22} & \cdots & \rho'_{2l} \\ \cdots & \cdots & \cdots & \cdots \\ \rho'_{la} & \rho'_{l2} & \cdots & \rho'_{ll} \end{vmatrix}^*$$

$$= H_c^1(x_a)\rho_{a1'} + \sum_{l=2}^{6} \frac{N!}{(N-l)!\,(l-1)!} \times \int \Psi(x_1 x_2 \ldots x_N) H_c^l(x_a x_2 \ldots x_l) \times \Psi^*(x_a x_2 \ldots x_N) dx_2 \ldots dx_N$$

$$= H_c^1(x_a)\rho_{a1'} + \sum_{l=2}^{6} \frac{N!}{(N-l)!\,(l-1)!} \times \int \Psi^*(x_a x_2 \ldots x_N) H_c^l(x_a x_2 \ldots x_l) \times \Psi(x_1 x_2 \ldots x_N) dx_2 \ldots dx_N \tag{42}$$

since H_c^l is a real operator.

Thus we have

$$\text{R.H.S.} = H_c^1(x_a)\rho_{a1'} + \sum \frac{1}{(l-1)!} \int H_c^l(x_a \ldots x_l) dx_2 \ldots dx_l \times \begin{vmatrix} \rho'_{a1} & \rho'_{a2} & \cdots & \rho'_{al} \\ \rho'_{21} & \rho'_{22} & \cdots & \rho'_{2l} \\ \cdots & \cdots & \cdots & \cdots \\ \rho'_{l1} & \cdots & & \rho'_{ll} \end{vmatrix}. \tag{43}$$

Now

$$(K\rho)_{a1} = \sum_{l=1}^{6} \frac{1}{(l-1)!} \int K^l(x_a, x_2)\rho'(x_2, x_1) dx_2$$

$$= \sum_{l=1}^{6} \frac{1}{(l-1)!} \{B^l(x_a)\rho'_{a1} + (l-1) \int H_c^l(x_a x_2 \ldots x_l) \times \rho'_{l;\,2a}\rho'_{21} dx_2 \ldots dx_l\}$$

$$= \text{R.H.S.} \tag{44}$$

as can be seen by expanding the determinants in (43) along their first columns. Thus the equation (32) is the $(a1)$-th element of $K\rho - \rho K$. Hence we can write

$$K\rho - \rho K = 0. \tag{45}$$

The second term in $K_l(x_2, x_1)$ subtracts from the matrix $B(x_2, x_1) = \delta(x_2 - x_1) B(x_1)$ the physically irrelevant terms corresponding to the action of an electron upon itself and at the same time accounts for the exchange effect.

We can in fact express the energy of the system in terms of the matrices $K^l(x_1, x_2)$ we have

$$W = D\left[\rho\left(\sum_{l=1}^{6} \frac{K^l}{l!}\right)\right] \tag{46}$$

where D denotes the diagonal sum or spur.

The matrix K is a generalisation of the matrix $(E + B - A)$ (*see* Frenkel, pages 428–36) for the case when correlation is introduced into the theoretical formalism, and reduces to the latter when correlation is neglected. It can thus be regarded as the energy matrix for the system in analogy with the theory of the density matrix based on the Hartree-Fock equations. The importance of the energy matrix lies in the facility with which it enables one to pass on to a representation in the phase space and thus to obtain a semi-classical expression for the density of the charge cloud of the system. It is well known that by transforming the matrix $K(x_1, x_2)$ into one $\{K(x_1, p_1)\}$ involving the position and momentum of the particles, one can obtain the so-called Thomas-Fermi-Dirac equation that includes exchange effects besides. Thus the matrix $K(x_1, x_2)$ defined in (37) can be used as a convenient starting-point to derive the equation governing the charge cloud of a molecular system; the details of this transformation theory leading to a correlated Thomas-Fermi charge distribution will be published separately in a different paper.

6. A General Correlation Factor

In the above discussion, we have chosen a correlation factor which is a linear function of $f(r_{ij})$ where r_{ij} is the inter-electronic distance between the i-th and j-th electrons; each term of g thus contains the co-ordinates of two electrons only. While this type of correlation factor is the simplest to deal with and can certainly be expected to improve the H.F. equations, it does not take into account of the multiple correlations connecting the

positions of different electrons at the same time. A general correlation function is either a polynomial in the $\binom{N}{2}$ inter-electronic distances or a convergent power series in them. Let us suppose that H_c $(= gHg)$ is of the form

$$H_c = \sum_{l=1}^{N} \left\{ \sum_{\sigma_1 \ldots \sigma l} \frac{1}{l!} H_c{}^l (x_1, x_2, \ldots, x_l) \right\}. \tag{47}$$

The correlated H.F. equations in this case become

$$\sum_{l=1}^{N} \frac{1}{(l-1)!} \int H_c{}^l (x_1, x_2, \ldots, x_l) \sum_{j=1}^{l} \rho'_{l;\,ij} \psi_k (x_j)\, dx_2 \ldots dx_l$$

$$- \sum_{i=1}^{N} \lambda_{ki} \psi_i (x_1) = 0 \qquad (k = 1, 2, \ldots, N). \tag{48}$$

The difference between (48) and (26) consists only in the summation for l; while in (26) the summation for l runs from 1 to 6, in (48), it runs from 1 to N. The integro-differential equations satisfied by the density matrices in this case can be obtained from (31) and (32) by making the summation for l to run from 1 to N.

7. Special Case

In this section, we write down the explicit form of the correlated H.F. equations for the case of the simplest two-electron system, namely the Helium atom. We do not propose to evaluate the energy of the system as this has been done by several authors, but give the form of the equations (26) as this might enable one to have some insight into the meaning of these equations. We have here

$$H_c{}^1 = \alpha^2 E (x_1) = \alpha^2 \left\{ \frac{p_1{}^2}{2m} - \frac{Ze^2}{r_1} \right\}$$

$$H_c{}^2 (x_1, x_2) = \alpha^2 F (x_1, x_2) + \alpha\beta \left[f(r_{12}), E (x_1) + E (x_2) \right]$$

$$+ \frac{2\alpha\beta e^2 f (r_{12})}{r_{12}} + \beta^2 f (r_{12}) \left[E (x_1) + E (x_2) \right] f (r_{12})$$

$$+ \frac{\beta^2 e^2 f^2 (r_{12})}{r_{12}}. \tag{49}$$

Equations (28) become

$$\mathrm{H_c}^1(x)\,\psi_1(x_1) + [\int \mathrm{H_c}^2(x_1, x_2)\,\psi_2^2(x_2)\,dx_2]\,\psi_1(x_1) - [\int \mathrm{H_c}^2(x_1, x_2)\,\psi_2^*(x_2)\,\psi_1(x_2)\,dx_2]\,\psi_2(x_1) = \mathrm{E}_1\psi_1(x_1) \tag{50}$$

and a similar equation for electron 2 which may be obtained from the above by interchanging the indices 1 and 2. In the above we have chosen a diagonal representation for the matrix (λ_{ij}), and E_1 and E_2 denote the diagonal elements. $\mathrm{H_c}^1$ denotes the kinetic energy operator of the electron 1 *plus* its potential energy in the field of the nuclei. The second term in the bracket gives the average of the operator $\mathrm{H_c}^2(x_1, x_2)$ for all positions of the electron 2 and the third term gives the exchange effects. Since $\mathrm{H_c}^2(x_1, x_2)$ contains a term $a^2\mathrm{F}(x_1, x_2)$, the part of it containing the factor a^2 can be interpreted as the potential energy of electron 1 moving in the average electric field of electron 2. The terms $a\beta\,[f(r_{12}), \mathrm{E}(x_1) + \mathrm{E}(x_2)]$ give the influence of correlation on the kinetic energies of the electrons. The term $[a\beta \int f(r_{12})\,\psi_2^2(x_2)\,dx_2]\,\mathrm{E}(x_1)$ especially shows that the kinetic energy of electron 1 is not independent of the motion of the electron 2, but is correlated with it. Since correlation reduces the chances of two electrons coming close to each other, it also reduces the fluctuations in the kinetic energies of the electrons and thus tends to make the distributions of the kinetic energies rather uniform. If we take $f(r_{12}) = r_{12}$, then $a\beta \int f(r_{12})/r_{12}\,\psi_2^2(x_2)\,dx_2 = a\beta$ and therefore the Hamiltonian for the electron 1 contains a constant term. By transferring this term to the right-hand side, the latter becomes $(\epsilon_1 - a\beta e^2)\,\psi_1$ and thus the influence of the correlation factor is to reduce the energy of the system. Since $f(r_{12})$ is an increasing function of r_{12}, the effect of the term $\beta^2 e^2 f^2(r_{12})/r_{12}$ in $\mathrm{H_c}^2(x_1, x_2)$ will be to increase the average inter-electronic distance and consequently to diminish the energy of the system.

8. Non-Stationary Systems

There are several problems of physical and chemical importance that depend for their solution on the time-dependent Schroedinger equation

$$\left(\mathrm{H} + \frac{h}{2\pi i}\frac{\partial}{\partial t}\right)\chi = 0. \tag{51}$$

In this section, we consider such non-stationary systems and find out the orbitals $\psi_k(x, t)$ that make the function $\Phi = g\Psi$, where Ψ is given by

(3 *a*), the 'best' approximation for the equation (51). These orbitals are given by the variational principle

$$\delta \int \Phi^* \left(\mathrm{H} + \frac{h}{2\pi i} \frac{\partial}{\partial t} \right) \Phi d\tau = 0 \tag{52}$$

or

$$\delta \int \Psi^* \left(\mathrm{H_c} - i\hbar \mathrm{G} \frac{\partial}{\partial t} \right) \Psi d\tau = 0 \tag{52 a}$$

where

$$\mathrm{G} = g^2$$

$$= a^2 + \frac{1}{2!} \sum_{ij}{}' \mathrm{G}(i,j) + \frac{1}{3!} \sum_{ijk}{}' \mathrm{G}(i,j,k)$$

$$+ \frac{1}{4!} \sum_{ijkl} \mathrm{G}(i,j,k,l) \tag{53}$$

$$\mathrm{G}(i,j) = 2a\beta f(r_{ij}) + \beta^2 f^2(r_{ij});$$

$$\mathrm{G}(i,j,k) = 2\beta^2 \left[f(r_{ij}) \left\{ \left(f(r_{jk}) + f(r_{ik}) \right) + f(r_{jk}) f(r_{ik}) \right\} \right];$$

$$\mathrm{G}(i,j,k,l) = 2\beta^2 \{ f(r_{ij}) f(r_{kl}) + f(r_{ik}) f(r_{jl}) + f(r_{il}) f(r_{jk}) \}. \tag{54}$$

We shall now evaluate the variation in (52 *a*) in two steps: first find out the variation of $\mathrm{J_1} = \int \Psi^* \mathrm{H_c} \Psi d\tau$ and secondly calculate the variation of

$$\mathrm{J_2} = \int \mathrm{G} \Psi^* \frac{\partial \Psi}{\partial t} d\tau. \tag{55}$$

(*a*) First consider

$$\delta \mathrm{J_1} = \int \delta\Psi^* \mathrm{H_c} \Psi d\tau + \int \delta\Psi \mathrm{H_c} \Psi^* d\tau. \tag{56}$$

Now $\int \Psi^* \mathrm{H_c} \Psi d\tau$ is given by (22) and $\int \delta\Psi^* \mathrm{H_c} \Psi d\tau$ can be obtained from this by varying only the primed quantities (or the quantities with an aesterisk) without varying $\psi_1, \psi_2, \ldots, \psi_\mathrm{N}$. We shall denote variations of this type by δ^*. Similarly $\int \delta\Psi \mathrm{H_c} \Psi^* d\tau$ can be obtained by replacing the Γ's in (22) by their complex conjugates and varying only the functions $\psi_1, \psi_2, \ldots, \psi_\mathrm{N}$ in $\Gamma^*(x_1' x_2' \ldots x_l' \mid x_1 \ldots x_l)$ $(l = 1, 2, \ldots, 6)$. As mentioned earlier we follow the convention that the operators $\mathrm{H_c}^l$ and $\partial/\partial t$ operate only on the unprimed quantities and that after these operations have been performed one should put $x_i' = x_i$ $(i = 1, 2, \ldots, \mathrm{N})$ and $t' = t$ in the integrals.

Since by (8 *a*) the Γ's are functions of ρ'_{ij}, we have

$$\delta^* \Gamma(x_1' x_2' \ldots x_l' \mid x_1 \ldots x_l) = \sum_{ij} \frac{\partial \Gamma(x_1' \ldots x_l' \mid x_1 \ldots x_l)}{\partial \rho'_{ij}} \delta^* \rho'_{ij}$$

$$= \frac{1}{l!} \sum_{i,j=1}^{l} \rho'_{l;ij} \left(\sum_{k=1}^{N} \delta\psi_k^*(x_i') \psi_k(x_j) \right) \tag{57}$$

where $\rho'_{l;ij}$ is the co-factor of ρ'_{ij} in ρ'_l.

Now

$$\int \delta\Psi^* \mathrm{H}_c \Psi \, d\tau$$

$$= \delta^* \sum_{l=1}^{6} \int \mathrm{H}_c{}^l(x_1 \ldots x_l) \, \Gamma(x_1' \ldots x_l' \mid x_1 \ldots x_l) \, dx_1 \ldots dx_l$$

$$= \sum_{l=1}^{6} \int \mathrm{H}_c{}^l(x_1 \ldots x_l) \sum_{i,j=1}^{l} \rho'_{l;ij} \left\{ \sum_{k=1}^{N} \delta \psi_k^*(x_i') \psi_k(x_j) \right\} \times dx_1 \ldots dx_l$$

$$= \sum_{l=1}^{6} \frac{1}{l!} \int \mathrm{H}_c{}^l(x_1 \ldots x_l) \times \left\{ \sum_{j=1}^{l} \rho'_{l;1j} \sum_{k=1}^{N} \delta \psi_k^*(x_1') \psi_k(x_j) + \sum_{i=2}^{l} \sum_{j=1}^{l} \rho'_{l;ij} \sum_{k=1}^{N} \delta\psi_k^*(x_i') \psi_k(x_j) \right\}. \tag{58}$$

Now the terms corresponding to the cases $i = 2, 3, \ldots, l$ can all be obtained from the first term of the above bracket by means of the cyclic permutations (x_1, x_2); (x_1, x_3); $\ldots$ (x_1, x_l) of the integration variables and thus the sums corresponding to the cases $i = 2, 3, \ldots, l$ are all identical with the sum corresponding to the case $i = 1$. Thus

$$\int \delta\Psi^* \mathrm{H}_c \Psi \, d\tau = \sum_{l=1}^{6} \frac{1}{(l-1)!} \int \mathrm{H}_c{}^l(x_1 \ldots x_l) \times \left\{ \sum_{j=1}^{l} \sum_{k=1}^{N} \rho'_{l;1j} \, \delta\psi_k(x_1') \psi_k(x_j) \right\} dx_1 \ldots dx_l \tag{59}$$

A similar expression follows for $\int \delta\Psi H_c \Psi^* \, d\tau$ in which the variation acts on the unasterisked quantities alone. Thus

$$\delta J_1 = \sum_{l=1}^{6} \frac{1}{(l-1)!} \int \sum_{j=1}^{l} \sum_{k=1}^{N} \delta\psi_k^* (x_1) \times \{H_c^{\,l} (x_1 \ldots x_l) \rho'_{l;\,1j} \psi_k (x_j) \, dx_1 \ldots dx_l\} + \int \delta\Psi H_c \Psi^* \, d\tau. \tag{60}$$

(*b*) Next we have

$$\delta J_2 = \int G \delta\Psi^* \frac{\partial \Psi}{\partial t} \, d\tau - \int G \delta\Psi \frac{\partial \Psi^*}{\partial t} \, d\tau. \tag{61}$$

Now

$$\begin{aligned} \delta^* \int G\Psi^* \frac{\partial \Psi}{\partial t} \, d\tau &= a^2 \sum_{k=1}^{N} \int \delta\Psi_k^* (x_1, t) \frac{\partial \Psi_k (x_1, t)}{\partial t} \, dx_1 \\ &+ \sum_{l=2}^{4} \delta^* \frac{1}{l!} \int G (x_1 \ldots x_l) \frac{\partial \rho'_{l+1}}{\partial t} \, dx_1 \ldots dx_{l+1} \\ &+ \sum_{l=2}^{4} \frac{(N-l-1)}{l!} \delta^* \int G (x_1 \ldots x_l) Q_{l+1} \, dx_1 \ldots dx_{l+1}, \end{aligned} \tag{62}$$

where

$$Q_{l+1} = \begin{vmatrix} \rho_{11} & \rho_{12} & \cdots & \rho_{1l+1} \\ \rho_{21} & \rho_{22} & \cdots & \rho_{2l+1} \\ \cdots & \cdots & \cdots & \cdots \\ \rho_{l1} & \rho_{l2} & \cdots & \rho_{ll+1} \\ \dfrac{\partial \rho'_{l+1,\,1}}{\partial t} & \cdots & \dfrac{\partial \rho'_{l+1,\,l}}{\partial t} & 0 \end{vmatrix} \tag{63}$$

$$= a^2 \sum_{k=1}^{N} \int \delta\psi_k^* (x_1, t) \frac{\partial \psi_k (x_1, t)}{\partial t} \, dx_1 + t_2 + t_3 \tag{64}$$

where t_2 and t_3 denote respectively the second and third terms in the above expression. We shall first consider t_2. We have

$$t_2 = \sum_{l=2}^{4} \frac{1}{l!} \delta^* \int G(x_1 \ldots x_l) \frac{\partial \rho'_{l+1}}{\partial t} dx_1 \ldots dx_{l+1}$$

$$= \sum_{l=2}^{4} \frac{1}{l!} \int G(x_1 \ldots x_l) \frac{\partial}{\partial t} \delta^* \rho'_{l+1} dx_1 \ldots dx_{l+1}$$

$$= \sum_{l=2}^{4} \frac{1}{l!} \int \begin{matrix} G(x_1 \ldots x_l) \\ dx_1 \ldots dx_{l+1} \end{matrix}$$

$$\times \frac{\partial}{\partial t} \left\{ \sum_{i=1}^{l+1} \sum_{j=1}^{l+1} \rho'_{l+1;\, ij} \sum_{k=1}^{N} \delta\psi_k^*(x_i') \psi_k(x_j) \right\}. \qquad (65)$$

Now the integrals of the sums corresponding to the cases $i = 2, 3, \ldots, l$ are all identical with the integral for the case $i = 1$. Further let us interchange the integration variables x_1 and x_{l+1} in the sum corresponding to the case $i = l + 1$. Then we get

$$t_2 = \sum_{l=2}^{4} \frac{1}{l!} \int [lG(x_1 \ldots x_l) + G(x_2 \ldots x_{l+1}]$$

$$\times \sum_{k=1}^{N} \delta \psi_k^*(x_1) \frac{P^k{}_{l+1}}{\partial t} dx_1 \ldots dx_{l+1} \qquad (66)$$

where

$$P^k{}_{l+1} = \begin{vmatrix} \psi_k(x_1, t) & \psi_k(x_2, t) & \ldots & \psi_k(x_{l+1}, t) \\ \rho'_{21} & \rho'_{22} & \ldots & \rho'_{2l+1} \\ \ldots\ldots & \ldots\ldots & \ldots & \ldots\ldots \\ \rho'_{l+1,\,1} & \rho'_{l+1,\,2} & \ldots & \rho'_{l+1,\,l+1} \end{vmatrix}. \qquad (67)$$

Next

$$t_3 = \sum_{l=2}^{4} \frac{(N - l - 1)}{l!} \int \begin{matrix} G(x_1 \ldots x_l) \\ dx_1 \ldots dx_{l+1} \end{matrix}$$

$$\times \left\{ \sum_{i=1}^{l} \sum_{j=1}^{l+1} Q_{l+1;\, ij} \left(\sum_k \delta\psi_k^*(x_i) \psi_k(x_j) \right) \right.$$

$$\left. + \sum_{j=1}^{l} Q_{l+1;\, l+1,\, j} \left(\sum_k \delta\psi_k^*(x_{l+1}) \frac{\partial \psi_k(x_j)}{\partial t} \right) \right\}. \qquad (68)$$

Now

$$Q_{l+1;\, l+1,\, j} = \rho_{l+1;\, l+1,\, j}. \tag{69}$$

Interchange as before the variables x_{l+1} and x_1 in the second term in the bracket of the above integral. Then we get

$$t_3 = \sum_{l=2}^{4} \frac{(N-l-1)}{l!} \int \sum_{k=1}^{N} \delta\psi_k^*(x_1)\, dx_1 \ldots dx_{l+1}$$
$$\times \left\{ lG(x_1 \ldots x_l) \sum_{j=1}^{l+1} Q_{l+1;\, 1j}\, \psi_k(x_j) \right.$$
$$\left. + G(x_2 \ldots x_{l+1}) \sum_{j=1}^{l} \rho_{l+1;\, 1j} \frac{\partial \psi_k(x_j)}{\partial t} \right\}. \tag{70}$$

(*c*) Thirdly the orbitals $\psi_i(x)$ satisfy the orthonormality conditions

$$\int \psi_k^*(x_1)\, \psi_i(x_1)\, dx_1 = 0 \tag{71}$$

or

$$\lambda_{ki} \int \delta\psi_k^*(x_1)\, \psi_i(x_1)\, dx_1 + \lambda_{ki} \int \psi_k^*(x_1)\, \delta\psi_i(x_1)\, dx_1 = 0$$
$$(i, k = 1, 2, \ldots, N) \tag{72}$$

where λ_{ki} are arbitrary constants.

Subtracting (72) from $\delta(J_1 - i\hbar J_2)$ which is given by (60), (64), (66) and (70) and equating to zero the coefficients of the variations $\delta\psi_k^*(x_1)$, we get

$$\left\{ H_c^{\,1}(x_1) - i\hbar\alpha^2 \frac{\partial}{\partial t} \right\} \psi_k(x_1) + \sum_{l=2}^{l} \frac{1}{(l-1)!}$$
$$\times \int H_c^{\,l}(x_1 \ldots x_l) \sum_{j=1}^{l} \rho'_{l;\, 1j}\, \psi_k(x_j)\, dx_2 \ldots dx_l$$
$$- i\hbar \sum_{l=2}^{4} \frac{1}{l!} \int \{ lG(x_1 \ldots x_l) + G(x_2 \ldots x_{l+1}) \}$$
$$\times \frac{\partial P^k_{l+1}}{\partial t}\, dx_2 \ldots dx_{l+1}$$
$$- i\hbar \sum_{l=2}^{4} \frac{(N-l-1)}{l!}$$

$$\times \int \left\{ lG(x_1 \ldots x_l) \sum_{j=1}^{l+1} Q_{l+1;\,1j}\, \psi_k(x_j) \right.$$

$$\left. + G(x_2 \ldots x_{l+1}) \sum_{j=1}^{l} \rho_{l+1;\,1j} \frac{\partial \psi_k(x_j)}{\partial t} \right\} dx_2 \ldots dx_{l+1}$$

$$= \sum_{i=1}^{N} \lambda_{ki}\, \psi_i(x_1) \qquad (73)$$

and a similar equation for the complex conjugate of $\psi_k(x_1)$.

In the above equation, the Lagrangian multipliers λ_{ki} are functions of time; further when correlation is neglected, (21) reduces to the time-dependent H.F. equations as can be seen by putting $\alpha = 1$ and $\beta = 0$.

Acknowledgment

The author's grateful thanks are due to Professor Sir C. V. Raman for his kind interest in this work and valuable suggestions.

Summary

The paper deals with a study of correlation effects in many-electron systems. Coulomb correlation is introduced into the theory by multiplying the Slater determinant formed from the one-electron orbitals by a correlation factor which is a symmetric and increasing function of the inter-electronic distances. The integro-differential equations satisfied by the best one-electron orbitals have then been deduced for non-stationary systems. From the extended Hart ee-Fock equations given by Löwdin, the integro-differential equations satisfied by the density matrices have been derived. An expression for the energy-matrix of the system which is helpful in deriving a correlated Thomas-Fermi charge distribution, has also been given.

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APPENDIX I

We shall here evaluate

$$T_l = \frac{\binom{N}{l}}{N!} \int G(x_1 x_2 \ldots x_l) \frac{\partial \rho'_N}{\partial t} dx_1 \ldots dx_N \tag{1}$$

and prove the relation (9) of Section 2. We have

$$T_l = \frac{\binom{N}{l}}{N!} \int \frac{G(x_1 x_2 \ldots x_l)}{dx_1 \ldots dx_N} \times \left\{ \sum_{i=1}^{l} \sum_{j=1}^{N} \rho_{N;ij} \frac{\partial \rho'_{ij}}{\partial t} + \sum_{i=l+1}^{N} \sum_{j=1}^{N} \rho_{N;ij} \frac{\partial \rho'_{ij}}{\partial t} \right\} \tag{2}$$

$$= T_1 + T_2 \text{ (say)} \tag{3}$$

where T_1 denotes the summation of i from 1 to 6 and T_2 denotes the sum of terms for $i = l+1$ to N. Since $G(x_1, \ldots, x_l)$ is a symmetric function of $x_1, \ldots, x_l$, the integrals of the sums corresponding to the terms $i = 2, 3, \ldots, l$ are all identical with the sum for the case $i = 1$. Thus

$$T_1 = \frac{\binom{N}{l}}{N!} \int lG(x_1 \ldots x_l) \sum_{j=1}^{N} \rho_{N;1j} \frac{\partial \rho'_{1j}}{\partial t} dx_1 \ldots dx_N. \tag{4}$$

Again the integrals corresponding to the cases $j = l+2, l+3, \ldots, N$ are all identical with the value of the integral for the case $j = l+1$, as can be seen by the transpositions of the integration variables (x_{l+1}, x_{l+2}); (x_{l+1}, x_{l+3}), $\ldots, (x_{l+1}, x_N)$. Further when $j < (l+2)$,

$$\int \rho_{N;1j} \, dx_{l+2} \ldots dx_N = (N-l)! \, \rho_{l+1;1j}. \tag{5}$$

Thus

$$T_1 = \frac{1}{l!} \int \frac{lG(x_1 \ldots x_l)}{dx_1 \ldots dx_{l+1}} \times \left\{ \sum_{j=1}^{l} \rho_{l+1;1j} \frac{\partial \rho'_{1j}}{\partial t} + (N-l) \, \rho_{l+1;1(l+1)} \frac{\partial \rho'_{1(l+1)}}{\partial t} \right\}. \tag{6}$$

We shall next consider T_2.

By means of the transpositions $(x_{l+1}\, x_{l+2}) \ldots (x_{l+1}, x_N)$ of the integration variables, one can see that the integrals corresponding to the cases $i = l+2$ to N are all identical with the value of the integral for $i = l+1$. Thus

$$T_2 = \frac{\binom{N}{l}}{N!}(N-l)\int G(x_1 \ldots x_l) \sum_{j=1}^{N} \rho_{N;\, l+1j} \frac{\partial \rho'_{l+1,j}}{\partial t}\, dx_1 \ldots dx_N \tag{7}$$

$$= \frac{\binom{N}{l}}{N!}(N-l)\int G(x_1 \ldots x_l) \times \left\{ \sum_{j=1}^{l+1} \rho_{N;\, l+1j} \frac{\partial \rho'_{l+1,j}}{\partial t} + (N-l-1) \times \rho'_{N;\, l+1,l+2} \frac{\partial \rho'_{l+1,l+2}}{\partial t} \right\} dx_1 \ldots dx_N \tag{8}$$

which follows again by the same argument of permutation of integration variables used above. Integrating the first term in the above with respect to the variables x_{l+2} to x_N and the second term with respect to the variables x_{l+3} to x_N one gets

$$T_2 = \frac{1}{l!}\int \frac{G(x_1 \ldots x_l)}{dx_1 \ldots dx_{l+1}} \times \left\{ (N-l) \sum_{j=1}^{l+1} \rho_{l+1;\, l+1,j} \frac{\partial \rho'_{l+1,j}}{\partial t} + (N-l-1) \times \rho_{l+2;\, l+1,l+2} \frac{\partial \rho'_{l+1,l+2}}{\partial t}\, dx_{l+2} \right\}. \tag{9}$$

Let us now consider the second term of the above expression and denote it by T_2^2. Expanding the determinant $\rho_{l+2;\, l+1,l+2}$ along its last column, integrating with respect to the co-ordinate of the electron $(l+1)$ and changing the integration variable x_{l+2} into x_{l+1} in the resulting integral, one gets

$$T_2^2 = -\frac{(N-l-1)}{l!}\int G(x_1 \ldots x_l)\, dx_1 \ldots dx_{l+1}$$

$$\times \left\{ l\rho_{l+1;\,1l+1} \frac{\partial \rho'_{1l+1}}{\partial t} + \frac{\partial \rho'_{l+1,\,l+1}}{\partial t} \rho'_{l+1;\,l+2,\,l+1} \right\}. \tag{10}$$

From (9), (10) and (6), we get on summing T_1 and T_2 and grouping together like terms that

$$\begin{aligned}(T_1 + T_2) = \frac{1}{l!} \int & lG(x_1 \ldots x_l) \\ & \times \left(\sum_{j=1}^{l+1} \rho_{l+1;\,1j} \frac{\partial \rho'_{1j}}{\partial t} \right) dx_1 \ldots dx_{l+1} \\ & + \frac{1}{l!} \int \frac{G(x_1 \ldots x_l)}{dx_1 \ldots dx_{l+1}} \\ & \times \left\{ (N-l) \sum_{j=1}^{l} \rho'_{l+1;\,l+1,\,j} \frac{\partial \rho'_{l+1,\,j}}{\partial t} \right. \\ & \left. + \rho'_{l+1;\,l+1,\,l+1} \frac{\partial \rho'_{l+1,\,l+1}}{\partial t} \right\} \end{aligned} \tag{11}$$

or

$$\begin{aligned} T_l = \frac{1}{l!} \int & G(x_1 \ldots x_l)\, dx_1 \ldots dx_{l+1} \\ & \times \left\{ \sum_{i=1}^{l} \sum_{j=1}^{l+1} \rho_{l+1;\,ij} \frac{\partial \rho'_{ij}}{\partial t} + \sum_{j=1}^{l+1} \rho_{l+1;\,l+1,\,j} \frac{\partial \rho'_{l+1,\,j}}{\partial t} \right. \\ & \left. + (N-l-1) \sum_{j=1}^{l} \rho_{l+1;\,l+1\,j} \frac{\partial \rho'_{l+1,\,j}}{\partial t} \right\}. \end{aligned} \tag{12}$$

On writing the summations in the above term in a determinental form, we get the relation (9) of Section 2.

INTENSITY STUDIES IN RAMAN EFFECT—POSITIONAL ISOMERISM

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1. Introduction

The infra-red absorption spectra of the various isomers of the *o*, *m*, *p* cresols, xylenes, ethyl toluenes and dichlorobenzenes have been investigated by Whiffen *et al.*[1] Their spectra reveal the existence of intense absorptions in the regions 700–800 cm.$^{-1}$ and 1200–1300 cm.$^{-1}$ The region 700–800 cm.$^{-1}$ is characteristic of benzenoid substances, with the substituents attached to the nucleus. It has been found that there is a shift of this 'aromatic band' towards higher frequencies in passing along the series *o-m-p* in most of the disubstituted benzenes regardless of the nature of the substituents.

The Raman spectra of the three isomeric cresols were investigated by Biswas,[2] in both liquid and solid states. The Raman spectra of *o-p*-chlorotoluenes and of *o-p*-xylenes in liquid and solid states were studied by Sanyal[3] and Biswas[4] respectively. According to Sanyal, *p*-chlorotoluene does not yield any line with a frequency below 306 cm.$^{-1}$ whereas there is an intense line at 163 cm.$^{-1}$ in the case of *o*-chlorotoluene. This line, he has attributed to the presence of dimers in *o*-chlorotoluene.

Very little work has been done in the case of these isomers with reference to the intensities of the Raman lines. A study of the frequencies and the intensities of the various Raman lines with reference to the position of the substitution has been attempted in the present investigation.

2. Experimental

Extra pure samples of the substances distilled at constant boiling-points have been used in the present investigation. A Hilger E 612 two-prism glass

spectrograph, in conjunction with a Raman Source Unit, was used. The spectra of each series have been recorded under identical conditions. A set of graded intensity marks were also given on the same plate and the intensities were computed using a Moll microphotometer.

3. RESULTS AND DISCUSSION

Tables I to IV contain the frequencies and the integrated intensities of the Raman lines in different isomers.

TABLE I

Xylenes

o-Xylene		*m*-Xylene		*p*-Xylene	
Frequency cm.$^{-1}$	Intensity	Frequency cm.$^{-1}$	Intensity	Frequency cm.$^{-1}$	Intensity
..	..	..	..	170	0·846
..	..	..	..	313	2·147
..	..	..	..	459	0·467
506	0·738	514	0·360	..	..
582	1·065	538	0·581	644	0·599
733	2·768	724	1·057	784	1·034
..	..	..	..	827	2·781
1051	0·936	..	..	1182	0·286
1222	2·452	..	..	..	..
1384	0·494	1375	0·414	1376	0·732
1606	0·780	1613	0·408	1606	0·768
..	..	2866	0·389	2860	3·081
2920	1·223	2916	1·982	2920	2·226
3047	1·999	3048	2·767	3052	1·414

TABLE II

Cresols

o-Cresol		*m*-Cresol		*p*-Cresol	
Frequency cm.$^{-1}$	Intensity	Frequency cm.$^{-1}$	Intensity	Frequency cm.$^{-1}$	Intensity
190	3·266	..	..	..	..
274	1·431	214 239	0·476	337	3·130
445	2·946	455	0·468	464	1·980
584	1·776	612	0·084	646	0·919
749	11·298	735 833	3·012 1·931	841	8·379
1044	4·407	1002 1042 1081	2·190 0·211 0·629	1100	0·227
1252	3·390	..	..	1251	2·083
1378	1·209	1378	0·772	1380	1·740
1400	2·625	1400	2·680	1400	2·638
1598 1620	2·396	1597 1614	3·549	1598 1612	4·873
2920	3·279	2929	2·292	2927	2·857
3057	3·922	3057	5·746	3048	6·850

From the results given in the above tables the following conclusions can be drawn: –

(1) The intensities of the corresponding lines are, in general, low in the *meta*-isomer.

(2) *In xylenes.*—(*a*) The strong line in the region 700–800 cm.$^{-1}$ represents the benzenoid vibration. According to Whiffen and Thompson this

TABLE III

Chloroanilines

o-Chloroaniline		*m*-Chloroaniline	
Frequency cm.$^{-1}$	Intensity	Frequency cm.$^{-1}$	Intensity
168	1·900	193	2·060
257	1·473	244	1·362
467	1·433	408	1·366
555	1·008	530	0·683
678	1·415	694	1·641
833	1·878	893	1·071
1020	1·843	1073	1·092
1304	2·231	1300	4·271

TABLE IV

Chlorotoluenes

o-Chlorotoluene		*p*-Chlorotoluene	
Frequency cm.$^{-1}$	Intensity	Frequency cm.$^{-1}$	Intensity
164	1·692	..	..
247	2·383	307	1·180
675	1·167	634	0·801
801	1·366	796	1·803
1040	1·243	1090	1·866
1204	0·947	1208	0·639
1590	1·545	1608	0·819
2920	1·149	2927	0·497
3062	1·543	3050	1·078

line in the infra-red appears at 743, 765 and 790 cm.$^{-1}$ in passing from *ortho*- to the *para*-compound. In the present investigation strong lines have been observed at 733 cm.$^{-1}$, 724 cm.$^{-1}$ and 784 cm.$^{-1}$ in the three isomers respectively, thus showing a diminution in frequency in the *meta*-isomer.

(*b*) The line in the region 2880–2860 cm.$^{-1}$ represents the symmetrical stretching of the methyl group attached to the benzene nucleus. This line has a maximum intensity in *para*, but it is very weak in *meta* and is absent in *ortho*-isomer.

(*c*) The line at 2916 cm.$^{-1}$, representing the asymmetrical stretching of the methyl group, shows a gradual increase in intensity from *ortho* to *para*-isomer.

(3) *In cresols.*—(*a*) Strong lines at 749, 735 and 841 cm.$^{-1}$ have been observed corresponding to the benzenoid vibration, while Whiffen and Thompson recorded it at 752, 775 and 827 cm.$^{-1}$ in the *o-m-p* cresols respectively.

(*b*) The intensities of the C–C vibration at 1000 cm.$^{-1}$ and the CH_3 asymmetric stretching in methyl attached benzene ring at 2916 cm.$^{-1}$ behave in the same way.

(*c*) No line has been observed in the region 2880–2860 cm.$^{-1}$ which represents the CH_3 symmetric stretching mode.

(4) *In chloroanilines.*—(*a*) There is a slight increase in intensity of the C–Cl vibration at 678 cm.$^{-1}$ in the *meta*-compound. This observation is different from what has been found in the other substances.

(*b*) The line at 1300 cm.$^{-1}$ in *meta*-isomer shows a doublet structure as a result of which the integrated intensity has been considerably enhanced.

(5) In chlorotoluenes the intensities of the lines in *ortho*-compound are greater than in the corresponding *para*-isomer.

The *para*-chloroaniline and *meta*-chlorotoluene were not investigated due to non-availability of the substances.

Since the vibrational intensity of a Raman band is a dependent function of the derivative of the polarisability, which is a related function of the electronic state of the bond, the observed variation in intensity in the three isomers may be explained, by considering the inductive effects brought into play by the various substituents attached to the benzene ring.

Shorygin[5] while studying the influence of the second substituent on the mono-derivatives of benzene has observed that the intensity of the first substituent depends upon the electronegativity of the second substituent group.

In the case of the intensity of the nitrogroup band, the intensity increases very sharply when electropositive radicals are introduced in the *para* position. He has also pointed out that the halogen atoms behave as electropositive groups as far as the intensity of the Raman scattering is concerned.

The compounds studied in the present investigation have the following groups: CH_3 groups in xylene; OH and CH_3 in cresols; NH_2 and Cl in chloroaniline; and CH_3 and Cl in chlorotoluene. All these groups are known to be electropositive. The degree of electronegativity is different for each group.

When an electropositive group like CH_3 is attached to the benzene ring, this group will force the electron into the ring due to the electron repelling character and consequently increases the electron density at the *ortho* and the *para* positions with respect to it and the effect at the *meta* is much less. If another methyl group is substituted in the *para* position, as in *para*-xylene, the positions *a* and *b* (Fig. 1) possess high electron density owing to the repulsive inductive effect of the alkyl group in the *ortho* position. Thus both the groups aid each other and the electron density will be increased.

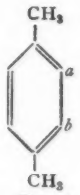

FIG. 1.

When the methyl group is attached to the *meta* position, due to cumulative effect of the electric charges induced in the *ortho* and the *para* positions, the electron density will be maximum.

In the *ortho* position, the inductive effects due to both the groups oppose each other and consequently change in the electron density induced in the ring will be minimum.

Thus it is seen that the changes in electron density induced in the ring follow the order *meta* > *para* > *ortho*. This will be the case with all the electropositive substituents though the changes may vary depending upon the degree to which they are electropositive. The observed results may thus qualitatively be explained on the basis that the increase in the electron density may cause a decrease in intensity of the Raman lines.

4. Summary

The Raman spectra of the *o-m-p* isomers of some substances have been investigated. It has been found that in all the cases the intensities of the corresponding Raman lines have a maximum value in the *ortho*-compound and a minimum value in the *meta*-isomer. An attempt has been made to explain the observed results on the basis of the change in electron density caused by the inductive effect of the various substituents attached to the benzene nucleus.

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SOLVENT EFFECT ON C ≡ N VIBRATION IN RAMAN EFFECT

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1. Introduction

The position of C ≡ N stretching vibration in nitriles has been extensively studied by various investigators,[1–3] and it is found that the above characteristic vibration occurs in the region of 2230 cm.$^{-1}$

The infra-red absorption study of solvent effect in relation to intermolecular forces has been made recently by Caldow *et al.*[4,5] They have pointed out that the variations in the vibrational spectrum may reveal alterations in the bond character caused by the particular type of intermolecular interaction and thus may even suggest a method of union between interacting partners.

A given vibrational chromophore may also show different behaviour according to the nature of the rest of the molecule in which it occurs. Jesson and Thompson[6] observed in the infra-red that on passing from vapour state to solutions in CCl_4 and $CHCl_3$, the C ≡ N group vibrational band of CH_3CN steadily increases in intensity whereas that of the C ≡ N group in CCl_3N steadily decreases. It has also been noticed that in these more complex cyanides C ≡ N group frequency is almost independent of the solvent although the band intensity varies considerably.

It has been observed by Caldow *et al.*[5] and Thompson and Steel[7] that the infra-red intensity of the C ≡ N vibration of benzonitrile in $CHCl_3$ is approximately double that of the same in CCl_4. A study of the solvent effect on the infra-red intensity of the C ≡N stretching vibration for some nitriles made by Foffani *et al.*[8] shows that the band intensities for the nitriles increase with the polarity of the solvent except in ketonitrile where the trend is reversed. They have attributed this difference in behaviour to the presence of two competing bond moments in ketonitriles.

It is clear from the above that, although some work has been done in infra-red, no work has been done regarding the study of the solvent effect on C ≡ N vibration in Raman effect. Accordingly, a study of the effect

of various types of solvents on this characteristic vibration of nitriles has been taken up in this investigation.

2. Experimental

All the liquids studied in the present investigation have been distilled at constant boiling-point before use. The Raman spectra of various mixtures (50% by volume concentration) have been photographed under identical conditions using Hilger Raman Source Unit along with E 612 Spectrograph. A set of intensity marks are also recorded on the same plate and the intensities estimated using the Moll recording type microphotometer.

3. Results and Discussion

The ratio of the integrated intensity of the C ≡ N frequency of benzo and acetonitriles in various solvents and the 458 cm.$^{-1}$ line of pure CCl_4, after applying the refractive index correction suggested by Woodward and George,[9] is calculated and the values thus obtained are presented in Table I.

Table I

Solvent (50% by vol. conc.) \ Solute	Benzonitrile 2224 cm.$^{-1}$	Acetonitrile 2250 cm.$^{-1}$
Pure ..	2·320	0·238
Carbon tetrachloride ..	1·172	0·092
Chloroform ..	0·940	0·078
Bromoform ..	0·172	0·103
Ethyl acetate ..	0·916	0·099
Methyl butyrate ..	0·512	0·106
Ethyl butyrate ..	0·913	0·100
Benzene ..	1·472	0·120
Toluene ..	1·349	0·122
Ethyl benzene ..	1·482	0·101
Chlorobenzene ..	1·425	0·133
Bromobenzene ..	1·318	0·104
Dioxan ..	1·269	0·096

From the results given in Table I, the following conclusions may be drawn:

(1) In the case of benzonitrile mixtures, the intensity of C ≡N vibration does not show any appreciable variation in the aliphatic non-polar solvent CCl_4 whereas it is considerably diminished in the aliphatic polar solvents. It shows an increase in intensity in the case of all the aromatic solvents studied.

(2) In the case of acetonitrile mixtures, the intensity of C ≡ N vibration does not show any variation in aromatic non-polar solvents like benzene and toluene. In both polar and non-polar aliphatic solvents and in polar aromatic solvents, in general, an appreciable diminution in intensity has been obtained.

(3) In heterocyclic non-polar solvent dioxan an increase in the intensity is noticed in benzonitrile mixtures while there is a decrease in intensity in acetonitrile mixtures.

Thus it may be inferred that the aliphatic and aromatic non-polar solvents have no effect on the aromatic and aliphatic nitriles respectively. In all other cases, the solvents may interact with the solutes thereby altering the bond length of the chromophoric group and hence affecting the polarisability derivative. This may probably be the reason for the variation of intensity noticed in those cases.

According to Caldow *et al.*, the C = O and C ≡ N groups should behave roughly in a similar fashion as regards interactions with solvent molecules. The observations made by Venkateswarlu and Ramaswamy[10] show that the ratio of the intensities of C = O vibration in CCl_4 and $CHCl_3$ solvents in general is found to be approximately 1 : 2 which is in good agreement with those made by Caldow *et al.* But in the present investigation the behaviour of C ≡ N vibration is found to be different from that of the same in the infra-red in the sense that the intensity of the line in CCl_4 is observed to be great when compared with that in $CHCl_3$, the ratio of the intensities being roughly 5 : 4.

4. SUMMARY

The effect of various solvents on the intensity of C ≡ N vibration of benzo and acetonitriles has been studied. It has been observed that the aliphatic and aromatic non-polar solvents have no effect on the aromatic and aliphatic nitriles respectively. In all other cases, a marked variation in intensity has been noticed. The intensity of C ≡ N vibration in Raman

effect shows a diminution when the solvent is changed from carbon tetrachloride to chloroform while it shows a considerable increase in infra-red.

One of the authors (C. B.) is thankful to the Government of India for the award of Senior Research Scholarship.

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A LIMITING PROCESS IN QUANTUM ELECTRODYNAMICS

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Abstract

It is shown that the interaction between two charged particles reduces to that of a potential with one particle when the mass of the other tends to infinity. Recoil corrections when one of the masses is finite and large is also estimated in the case of two fermion scattering and bremsstrahlung in two-fermion interaction.

1. Introduction

In classical mechanics it is well known that when two particles collide there is only a change of momentum without transfer of energy if one of the colliding particles has infinite mass. In electrodynamics the interaction of a charged particle with a potential is characterised by a change in momentum without any change in energy if it is assumed that the seat of the potential is stationary during the process. However if the potential were due to a particle of finite mass its motion will have to be taken into consideration and this implies an exchange of energy also. For example, this is the case in electron-electron scattering where the interaction occurs through the exchange of a virtual photon or equivalently through an instantaneous Coulomb potential and transverse photons. Hence it is found interesting to investigate whether in the case of a two-particle interaction when one of the masses tends to infinity the situation will reduce to that of an interaction with a potential. This is indeed found to be so in correspondence with the classical case of change of momentum without transfer of energy. If instead of assuming the mass of one of the particles to be infinite, we consider it to be large compared to the other, then we can obtain a recoil correction proportional to the ratio of the masses.

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2. Single Photon Exchange between Two Fermions

We shall first demonstrate that a two-fermion interaction reduces to a potential scattering of a fermion when the mass of the other tends to infinity. The Feynman diagram for the interaction of two fermions of masses m_1 and m_2 is given in Fig. 1.

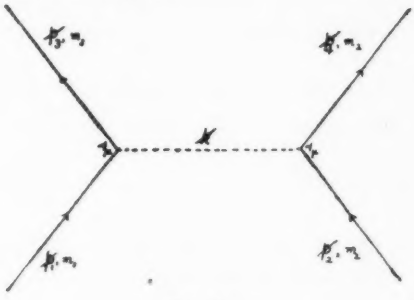

Fig. 1

The matrix element for this process is

$$M = 4\pi e^2 \sum_{\mu} \sum_{\text{Spins } 1,2,3,4} \left\{ [\bar{u}(p_3)\gamma_\mu u(p_1)] \frac{1}{k^2} [\bar{u}(p_4)\gamma_\mu u(p_2)] \right\}^1$$

with

$$\not{p}_3 - \not{p}_1 = \not{k} = \not{p}_2 - \not{p}_4 \tag{1}$$

which is the conservation law obtained from the space-time integration. From purely kinematical considerations, making use of these conservation laws it can be shown that if m_1 tends to infinity and the initial momentum $\vec{p}_1$ is zero, then the fourth component of the final four momentum p_3 is the same as that of p_1, *i.e.*, the rest mass. Hence the fourth component of the four momentum of the virtual photon is zero. However, taking m_1 to be finite and large compared to m_2 we find that $\vec{p}_3$ does not vanish and hence there is a recoil. This recoil correction is expressed conveniently in terms of the ratio of the masses which vanishes when m_1 tends to infinity. The square of the matrix element (1) reduces to

$$|M|^2 = \left[\frac{4\pi e^2}{\vec{k}^2}\right]^2 \left\{ \sum_{\mu} \frac{1}{2} \operatorname{Sp} \left[\gamma_\mu \frac{\not{p}_1 + m_1}{2E_1} \bar{\gamma}_\mu \frac{\not{p}_3 + m_1}{2E_3} \right] \right.$$

$$\left. \times \frac{1}{2} \operatorname{Sp} \left[\gamma_\mu \frac{\not{p}_2 + m_2}{2E_2} \bar{\gamma}_\mu \frac{\not{p}_4 + m_2}{2E_4} \right] \right\} \tag{2}$$

here is no recoil.

Hence the cross-section becomes

$$\sigma = \text{transition probability per second} \times 1/v$$

$$= \frac{1}{v} 2\pi \mid \mathrm{M} \mid^2 \rho\,(\mathrm{E})\, d\mathrm{E} \tag{3}$$

where v is the velocity of the particle $(= p/\mathrm{E})$ and $\rho\,(\mathrm{E})\,d\mathrm{E}$ the density of final states of the single particle.

Since $\mathrm{E}_2 = \mathrm{E}_4 = \mathrm{E}$ and $\mid p_2 \mid = \mid p_4 \mid = \mid p \mid$ and if θ is the angle between $\vec{p}_2$ and $\vec{p}_4$ we have

$$\sigma = \frac{4e^4\mathrm{E}^2}{k^4}\left[1 - v^2 \frac{\sin^2\theta}{2}\right]. \tag{4}$$

This is identical with the scattering cross-section of a particle by a potential. Thus we find that the second order process in a two-particle case reduces to a single scattering by a potential when the mass of one of the charged particles tends to infinity. The cross-section with recoil is given by

$$\sigma_{\text{recoil}} = \sigma\,(1 - \mathrm{X}) + \frac{4e^4 \cos\theta\, \mathrm{E}_4{}^2}{\left(\vec{k}^2\right)^2} \mathrm{X} \left\{1 + \mathrm{E}_4\left(1 - \frac{m_2{}^2}{2\mathrm{E}_4{}^2}\right)\right.$$

$$\left. \times \left(\frac{\mathrm{E}_4}{\mathrm{E}_2}\right) + \frac{m_2{}^2}{2\mathrm{E}_2{}^3} + \frac{m_2{}^2}{2\mathrm{E}_2{}^2\mathrm{E}_4}\right)\Bigg\} \tag{5}$$

and

$$\mathrm{X} = \epsilon \left\{\frac{1}{2m_2}\left[\mathrm{E}_4 + \frac{\mathrm{E}_2{}^2}{\mathrm{E}_4} + \mathrm{E}_2 \cos\theta\right]\right.$$

$$\left. - m_2\left(\frac{1}{\mathrm{E}_4} + \frac{\cos\theta}{2\mathrm{E}_2} + \frac{2\mathrm{E}_2 \cos\theta}{\mathrm{E}_4{}^2}\right) - \frac{m_2{}^3}{2\mathrm{E}_2\mathrm{E}_4{}^2}\right\}$$

where $\epsilon = m_2/m_1$ and terms of the order $1/m_1{}^2$ have been neglected.

3. Two-Photon Exchange between Two Fermions[2]

We now consider the process of higher order where two photons are exchanged between two fermions. The two possible Feynman diagrams are given in Fig. 2.

The matrix element can be written down as usual. But in this case an integration over the four momentum k of the photon also occurs. This is due to the fact that there are two virtual photons exchanged and the

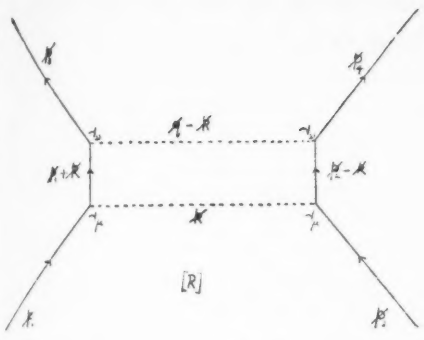

FIG. 2 *a*

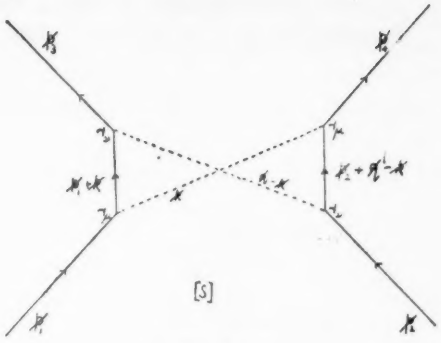

FIG. 2 *b*

given transfer of momentum between the two fermions can be shared in any ratio between the two photons. The net transfer of energy between the two fermions is zero in the limit m_1 tending to infinity and this gives rise to the factor $\delta(q_4)$ in the matrix element. Thus the matrix element for the R diagram is

$$M_R = \left[\frac{e^2}{\pi i}\right]^2 \sum_{\mu,\nu} \sum_{\text{Spins 1, 2, 3, 4}} \times \left\{ \int \left[\bar{u}(p_3)\gamma_\nu \frac{\not{p}_1 + \not{k} + m_1}{(p_1 + k)^2 - m_1^2}\gamma_\mu u(p_1)\right] k^2 (q-k)^2 \right. \times \left. \left[\bar{u}(p_4)\gamma_\nu \frac{\not{p}_2 - \not{k} + m_2}{(p_2 - k)^2 - m_2^2}\gamma_\mu u(p_2)\right]\right\} d^4k \quad (6)$$

This integral is divergent but can be evaluated by the usual technique[3] of introducing a small negative imaginary part $i\epsilon$ and making ϵ tend to zero and also the convergence factor $\lambda^2_{\min}$. Thus

$$M_R = \left[\frac{e^2}{\pi i}\right]^2 \sum_{\mu,\nu} \sum_{\text{Spins 1, 2, 3, 4}} \times \left\{ \int \left[\bar{u}(p_4)\gamma_\nu \frac{\not{p}_2 - \not{k} + m_2}{(p_2 - k)^2 - m_2^2}\gamma_\mu u(p_2)\right] \frac{dk_4}{2k_4} \right. \times \left. \frac{d^3k}{(k^2 - \lambda^2_{\min})[(q-k)^2 - \lambda^2_{\min}]} \right. \quad (7)$$

It is to be noted that $\vec{q}$ is only a three vector in this expression (7) since the conservation laws give rise to the factor $\delta(q_4)$.

The corresponding Feynman diagrams for the double scattering of a fermion due to a potential are given in Fig. 3.

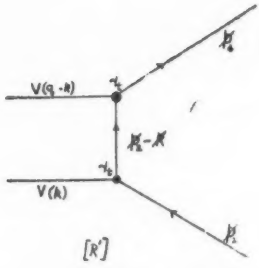

FIG. 3 *a*

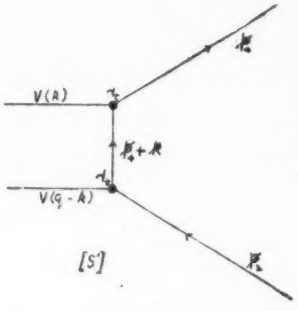

FIG. 3 *b*

The matrix element for the R′ diagram is

$$M_{R'} = \frac{e^4}{\pi i} \sum_{\text{Spins 2, 4}} \int \left[\bar{u}(p_4) \cdots t \frac{\not{p}_2 - \not{k} + m_2}{(p_2 - k)^2 - m_2^2} \cdots t u(p_2) \right]$$

$$\times \frac{d^3k}{\left(\vec{k}^2 - \lambda^2_{\text{min.}}\right)\left((q-k)^2 - \lambda^2_{\text{min.}}\right)} . \tag{8}$$

Here the integration is only three dimensional because the conservation laws yield the factor $\delta(k_4)\,\delta(q_4 - k_4)$. It can be shown that expressions (8) and (7) are identical by carrying out the integration over k_4 in (7). This is performed by taking the principal value of the integral which is equal in magnitude and opposite in sign to that obtained by performing the integration along a semicircle of radius ϵ around to pole $k_4 = 0$ as $\epsilon \to 0$, provided there are no poles in the upper half plane as is the case here. Thus we have

$$-\frac{1}{\pi i} \int \frac{dk_4}{k_4} = \delta(k_4).$$

Hence the expressions (8) and (7) are identical. Similarly it can be shown that M_S and $M_{S'}$ become identical in the limit $m_1 \to \infty$ and thus two-photon exchange is found to be equivalent to double scattering by a potential in this limit.

4. Bremsstrahlung in Two-Fermion Interaction

In this process we shall demonstrate that bremsstrahlung becomes more important as the mass of one the particle increases and in the limit $m_1 \to \infty$, the process reduces to a pure bremsstrahlung. The Feynman diagrams are shown in Fig. 4.

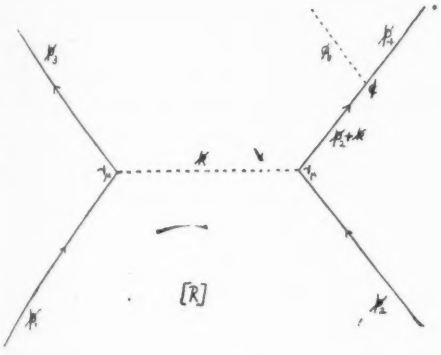

Fig. 4 *a*

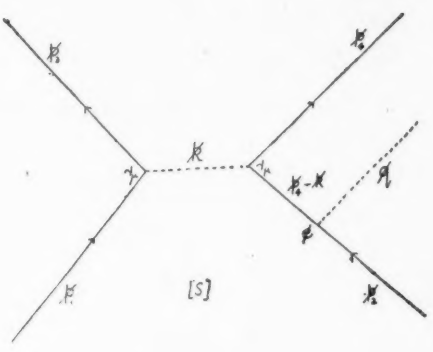

Fig. 4 *b*

The matrix element for the R diagram is given by:

$$M_R = 4\pi e^2 \sum_{\mu} \sum_{\text{Spins } 1,2,3,4} \left\{ [\bar{u}(p_3)\gamma_\mu u(p_1)] \times \frac{1}{k^2}\left[\bar{u}(p_4) \not{\epsilon} \frac{\not{p}_2 + \not{k} + m_2}{(p_2+k)^2 - m_2^2}\gamma_\mu u(p_2)\right]\right\}. \tag{9}$$

The square of the matrix element is then given by

$$|M_R|^2 = \left[\frac{4\pi e^2}{k^2}\right]^2 \left\{ \sum_{\mu} \frac{1}{2} \text{Sp}\left[\not{\epsilon} \frac{\not{p}_2 + \not{k} + m_2}{(p_2+k)^2 - m_2^2} \times \gamma_\mu \frac{\not{p}_2 + m_2}{2E_2} \bar{\gamma}_\mu \frac{\not{p}_2 + \not{k} + m_2}{(p_2+k)^2 - m_2^2} \bar{\not{\epsilon}} \frac{(\not{p}_4 + m_2)}{2E_4}\right] \times \frac{1}{2} \text{Sp}\left[\gamma_\mu \frac{\not{p}_1 + m_1}{2E_1} \bar{\gamma}_\mu \frac{\not{p}_3 + m_1}{2E_3}\right]\right\}$$

$$= \left[\frac{4\pi e^2}{k^2}\right]^2 \left\{ \sum_{\mu} \frac{1}{2} \; Sp \left[\not{\epsilon} \frac{\not{p}_2 + \not{k} + m_2}{(p_2 + k)^2 - m_2^2} \gamma_\mu \frac{\not{p}_2 + m_2}{2E_2} \right.\right.$$

$$\left.\left. \times \bar{\gamma}_\mu \frac{\overline{\not{p}_2 + \not{k} + m_2}}{(p_2 + k)^2 - m_2^2} \bar{\not{\epsilon}} \frac{\not{p}_4 + m_2}{2E_4} \right] \left[1 + \frac{\delta}{2m_1}\right] \right\} \quad (10)$$

where δ is the increase in energy of the mass m_1. In the limit $m_1 \to \infty$, the factor $\delta(k_4)$ can be obtained as in the case of single photon exchange and the four vector k reduces to $\vec{k}$.

The Feynman diagrams for ordinary bremsstrahlung process are given in Fig. 5.

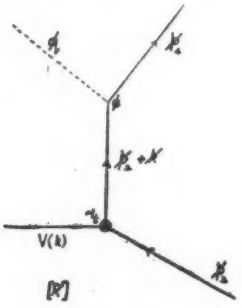

FIG. 5a

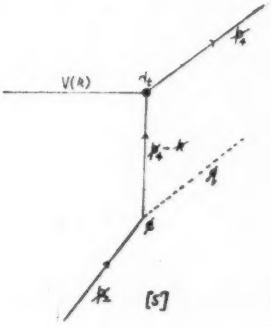

FIG. 5b

The matrix element of R′ diagram is

$$M_{R'} = \left[\frac{4\pi e^2}{\vec{k}^2}\right] \left\{ \sum_{\text{Spins } 2,4} \bar{u}(p_4) \not{\epsilon} \frac{\not{p}_2 + \not{k} + m_2}{(p_2 + k)^2 - m_2^2} \gamma_t u(p_2) \right\}. \quad (11)$$

Or, the square of the matrix element is

$$|M_{R'}|^2 = \left[\frac{4\pi e^2}{\vec{k}^2}\right]^2 \left\{ \frac{1}{2} \; Sp \left[\not{\epsilon} \frac{\not{p}_2 + \not{k} + m_2}{(p_2 + k)^2 - m_2^2} \right.\right.$$

$$\left.\left. \times \gamma_t \frac{\not{p}_2 + m_2}{2E_2} \bar{\gamma}_t \frac{\overline{\not{p}_2 + \not{k} + m_2}}{(p_2 + k)^2 - m_2^2} \bar{\not{\epsilon}} \frac{\not{p}_4 + m_2}{2E_4} \right] \right\}. \quad (12)$$

On carrying out the spur calculations it is found that the expressions (10) and (12). Similarly the limiting forms of $|M_S|^2$ and $|M_{S'}|^2$ will turn

out to be identical. Thus we find that bremsstrahlung in a two-fermion interaction reduces exactly to ordinary bremsstrahlung in this limiting case.

The cross-section taking into account the recoil, *i.e.*, when m_1 is large and finite, is given by

$$\sigma_{\text{recoil}} = \sigma_{\text{B.S.}} \left[1 + \text{XE}_4 \frac{2\text{E}_2}{\left[\vec{k}^2 + 2\vec{p}_2 \cdot \vec{k}\right]} - \frac{2\text{E}_4}{\left(\vec{k}^2 - 2\vec{p}_4 \cdot \vec{k}\right)} \right]$$

$$+ \frac{1}{2\pi} \left[\frac{e^2}{\vec{k}^2} \right]^2 e^2 \frac{dq_4}{q_4} \frac{p_4}{p_2} \sin\theta_2 d\theta_2 \sin\theta_1 d\theta_1 d\phi \frac{\text{XE}_4}{2}$$

$$\times \left\{ \frac{-2\text{E}_2{}^2\text{E}_4 - 2m_2{}^2\text{E}_4 + 2m_2{}^2\text{E}_2}{\left(\vec{k}^2 + 2\vec{p}_2 \cdot \vec{k}\right)^2} \right.$$

$$+ \frac{2\text{E}_4{}^2\text{E}_2 + 2m_2{}^2\text{E}_2 - 2m_2{}^2\text{E}_4}{\left(\vec{k}^2 - 2\vec{p}_4 \cdot \vec{k}\right)^2}$$

$$\left. + 2 \frac{[m_2{}^2\text{E}_4 - m_2{}^2\text{E}_2 - \text{E}_2\text{E}_4(\text{E}_2 + \text{E}_4)]}{\left(\vec{k}^2 + 2\vec{p}_2 \cdot \vec{k}\right)\left(\vec{k}^2 - 2\vec{p}_4 \cdot \vec{k}\right)} \right\} \tag{13}$$

where $\sigma_{\text{B.S.}}$ is the normal bremsstrahlung cross-section and X, the expression defined previously.

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[1] Throughout this paper we use the following notation. We denote the four vector p by p and the three vector by $\vec{p}$. The daggared operator $\not{p}$ is defined as $\not{p} = \gamma_1 p_1 - \gamma_2 p_2 - \gamma_3 p_3 - \gamma_4 p_4$ and the scalar product of two four vectors as $p_1 \cdot p_2 = p_{1t} p_{2t} - \vec{p}_1 \cdot \vec{p}_2$. We have also used the natural units $\hbar = c = 1$.

[2] We are grateful to Mr. A. P. Balachandran for suggesting this problem and drawing our attention to the fact that in spite of the crossing of photons in the four vertices the interaction in the limiting case should reduce to a second order scattering of a potential.

[3] Feynman, R. P., *Phys. Rev.*, 1949, **76**, 769.

CHARGE DISTRIBUTION OF THE PROTON

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Abstract

An expression for the charge density of proton is presented and the form factor calculated on the basis of this is compared with the experimental results. The results are also compared with those of the exponential model and the cut-off model of Hofstadter (1959).

Introduction

The experiments on the scattering of electrons by protons have yielded valuable information on the structure of the proton.[1] The experimental results are interpreted in terms of the Rosenbluth expression[2] for the scattering cross-section, modified by the introduction of the charge and the magnetic moment form factors F_1 and F_2.

$$\frac{d\sigma}{d\Omega} = \left(\frac{e^2}{2E_0}\right)^2 \frac{\cos^2\frac{\theta}{2}}{\sin^4\frac{\theta}{2}} \cdot \frac{1}{1+\frac{2E_0}{Mc^2}\sin^2\frac{\theta}{2}} \times \left\{F_1^2 + \frac{\hbar^2 q^2}{4M^2c^2}\left[2(F_1+KF_2)^2\tan^2\frac{\theta}{2} + K^2F_2^2\right]\right\} \quad (1)$$

where E_0 is the incident electron energy, M is the mass of the proton, $q = (2/\lambda)\sin\theta/2$ is the 4-momentum transfer and K is the anomalous magnetic moment of the proton. This formula is expected to be valid in the range of the electron energies and momentum transfers investigated at present. The phenomenological analysis of the data available is consistent with the simple assumption $F_1 = F_2 = F$, and that F may be interpreted in terms of a static charge distribution $\rho(r)$ as

$$F = \frac{4\pi}{q}\int_0^\infty \rho(r)\sin qr \,.\, rdr. \quad (2)$$

Several different charge distribution models may be written down, all of which give equally statisfactory fit to the experimental data. One of the best known is the exponential model which gives for the root-mean-square radius of the proton $0{\cdot}80 \times 10^{-13}$ cm. All other satisfactory models also give similar values. Hofstadter[3] has pointed out that although the simplest meson-theoretic model

$$\rho(r) = \frac{\rho_0 e^{-\alpha r}}{r^2} \tag{3}$$

is inadequate to fit the experimental data, this distribution modified for small values of r by the introduction of an additional cut-off parameter can satisfactorily fit the data. Hofstadter's model is given by

$$\left.\begin{aligned} \rho &= \rho_0 h \qquad 0 \leqslant r \leqslant d \\ \rho &= \frac{\rho_0 e^{-br}}{r^2} \qquad d \leqslant r \leqslant \infty \end{aligned}\right\} \tag{4}$$

and contains an unpleasant discontinuity at $r = d$. In view of the theoretical interest of such models we have explored further in an attempt to write down a satisfactory well-behaved charge distribution function. Such a function is described in §2, and the results are discussed in §3.

2. Results

The general aim is to change the expression (3) to

$$\rho(r) = \left[\frac{\rho_0 e^{-\alpha r}}{r^2}\right] \cdot f(r) \tag{5}$$

where $f(r)$ has suitable analytic properties. We require $f(r) \to 0$ for $r \to 0$, and $f(r) \to 1$ as $r \to \infty$, so that the divergence of $\rho(r)$ at $r = 0$ is removed, and piling up of charge at the centre of the proton is avoided. Our first attempt was to choose

$$f(r) = (1 - e^{-\beta r}). \tag{6}$$

It was however found that no choice of parameters α and β could produce a satisfactory fit to the experimental data.

Next, we have tried a modifying function of the type

$$f(r) = (1 - e^{-\beta r})^2 \tag{7}$$

as we wish to keep the charge-density positive at all values of r. This combined with (5) and (2) gives

$$F(q) = \left[\frac{a}{2q}(1+n)(2+n)\left\{\tan^{-1}\frac{q}{a} - 2\tan^{-1}\left(\frac{n}{n+1}\right)\frac{q}{a} + \tan^{-1}\left(\frac{n}{n+2}\right)\frac{q}{a}\right\}\right] \quad (8)$$

where $n = \alpha/\beta$.

Now F^2 *versus* q^2 is plotted for different values of α and β varied systematically. It is found that a satisfactory fit to the experimental data is obtained for

$$\alpha = \beta = 2{\cdot}557 \times 10^{13}\ \text{cm.}^{-1}$$

$$a^{-1} = 0{\cdot}39 \times 10^{-13}\ \text{cm.}$$

With these values of the parameters, one easily finds for the root-mean-square radius

$$a = 0{\cdot}85 \times 10^{-13}\ \text{cm.}$$

Figure 1 shows the comparison of the experimental values of F^2 and the values calculated on the above model. The errors on the experimental

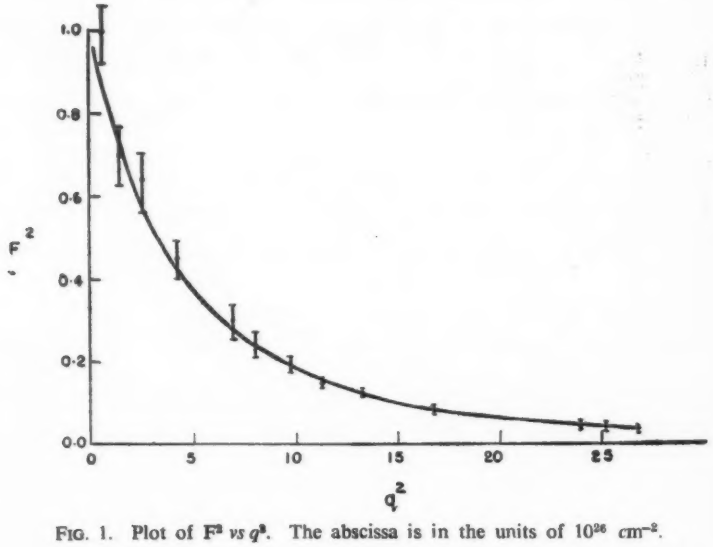

FIG. 1. Plot of F^2 *vs* q^2. The abscissa is in the units of 10^{26} cm^{-2}.

values are $\approx 10\%$. It can be seen that the agreement is quite good up to the highest momentum transfers yet observed, and a breakdown of the static

model is not yet in sight. The shape of the charge distribution $\rho(r)$ multiplied by r^2 is plotted against r in Fig. 2. Also shown r in this figure is the exponential charge distribution.

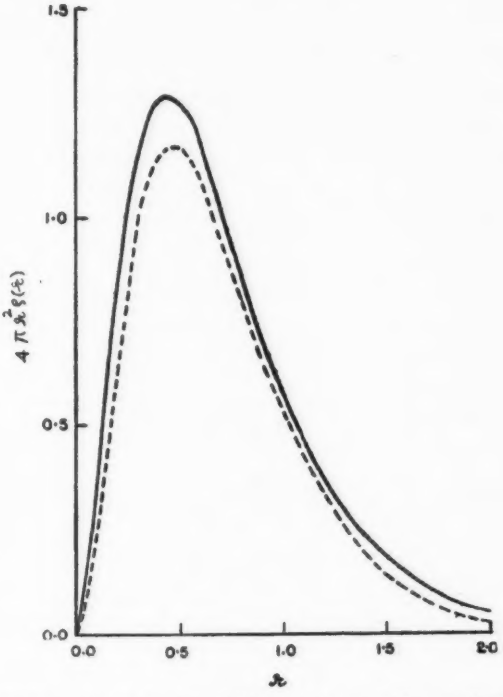

FIG. 2. Plot of $4\pi r^2 \rho(r)$ *vs.* r. The abscissa is in the units of 10^{-13} cm. The solid line represents the charge distribution model given by equations (5) and (7), and the dotted line gives the exponential model.

DISCUSSION

We shall now make a few remarks on the results described above. The values of a and a confirm the general trend of the results of Hofstadter. The root-mean-square radius is quite close to that obtained by other models, *viz.*, $0{\cdot}80 \times 10^{-13}$ cm. for the exponential model, and $0{\cdot}82 \times 10^{-13}$ cm. for the models given by equation (4). The value of the range parameter α^{-1} is larger than that obtained in the exponential model, but is comparable to the value $b^{-1} = 0{\cdot}4 \times 10^{-13}$ cm. obtained by Hofstadter for the models of equation (4). It is also clear that whatever the type of the modification introduced in the simple meson-theoretic charge distribution (3) for small

r it has to be operative for $r \leqslant 0{\cdot}4 \times 10^{-13}$ cm., as indicated by the value $d \approx 0{\cdot}4 \times 10^{-13}$ cm. found by Hofstadter and $\alpha = \beta$ obtained by us. At such distances, one would expect the simple π-meson cloud effects to be modified by the effects of the K-mesons ($\hbar/M_K c \approx 0{\cdot}4 \times 10^{-13}$ cm.) and the nucleon core ($\hbar/Mc = 0{\cdot}21 \times 10^{-13}$ cm.) structure. However, in view of the fact that the simple meson-theoretic model (3) would only be valid for $r \gtrsim 1 \times 10^{-13}$ cm. and the purely phenomenological approach of our model, it would be unwise to stress the discrepancy between the range-parameters obtained here ($0{\cdot}4 \times 10^{-13}$ cm.) and required by the meson theory ($0{\cdot}7 \times 10^{-13}$ cm.).

In view of the result $\alpha = \beta$, the expressions obtained from (6) and (7) would appear to be power series in exp. $(-\alpha r)$. However, in view of our observation that (6) is quite unsatisfactory, one is tempted to interpret (7) as indicating a modification of the simple meson-theoretic potential $\psi \sim \exp.(-\alpha r)/r$ to $\psi \sim \exp.(-\alpha r/2)\,[1 - \exp.(-\alpha r)]/r$ resulting from the effects of the proton structure.

Finally, we note that the charge distribution model obtained from equations (5) and (7) [but not that obtained from equations (5) and (6)] reduces to the exponential form exp. $(-\alpha r)$ for small values of r.

ACKNOWLEDGEMENT

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